THE AMERICAN MINERALOGIST, VOL. 42, NOVEMBER-DECEMBER 1957

IONIC DIFFUSION AND THE PROPERTIES OF QUARTZ*
I. THE DIRECT CURRENT RESISTIVITY

HENRY E. WENDEN, *Harvard University, Cambridge, Massachusetts.*†

ABSTRACT

The direct current resistivity of a number of Z-cut plates of natural quartz has been measured and the dependence of the axial resistivity upon temperature, field intensity, crystallographic orientation and time of passage of current investigated. The history of investigation of this property is summarized and previous results tabulated. The current flowing in a quartz plate under the influence of an electric field is complex, consisting of parts having characteristic time dependence and activation energies. The anomalous charging and discharging currents were investigated, and are considered to be the result of a reversible interfacial polarization having a relaxation frequency near 0.01–0.001 cycle/sec. The early surge current is connected with the migration of impurity ions and decays as a result of irreversible trapping and electrolytic exclusion of these ions. During the period of dominance of this current, quartz displays semiconductor behavior. Room temperature resistivity during this phase of conduction is of the order of 10^{13}–10^{19} ohm-cm, resistivity at 500° C. is of the order of 10^5 ohm-cm, and activation energy lies in the range 20–25 kcal./mole. After passage of current for over 500 hours, the steady-state mechanism is unmasked, yielding an activation energy of 35–40 kcal./mole, room temperature resistivity of the order of 10^{27} ohm-cm, and resistivity at 500° C. of about 5×10^9 ohm-cm. Quartz is shown to have a marked voltage coefficient of resistivity which varies with temperature and time of passage of current. This complex interdependence of the factors affecting the resistivity of quartz arises out of the common connection with the migration of impurity ions. Resistivity is a vectorial property but the exact nature of the dependence has not been completely investigated. Ionic diffusion in the equatorial direction has been observed, and has been demonstrated to play a part in the equatorial conductivity. Existing discrepancies and contradictions in reported values for the resistivity of quartz are shown to have their origin in the neglect of the factor of time of passage of current. When current is passed for a sufficiently long time to exhaust impurity ion connected mechanisms of conduction, the difference between axial and equatorial resistivity and the difference between different samples of quartz is of the same magnitude as the experimental error.

INTRODUCTION

Quartz is outstanding among minerals for the constancy of its physical properties. Except in those cases where numerous voids or inclusions are present, the density, indices of refraction and unit cell dimensions of clear quartz, and even of most colored varieties, show a remarkable consistency from sample to sample and locality to locality. A Harvard group (Frondel and Hurlbut (1953)), studying variations in these properties of quartz, found differences so minute as to require instrumental

---

* Contribution No. 383, Department of Mineralogy and Petrography, Harvard University, Cambridge, Massachusetts.

† Present Address: Department of Mineralogy, The Ohio State University, Columbus, Ohio.

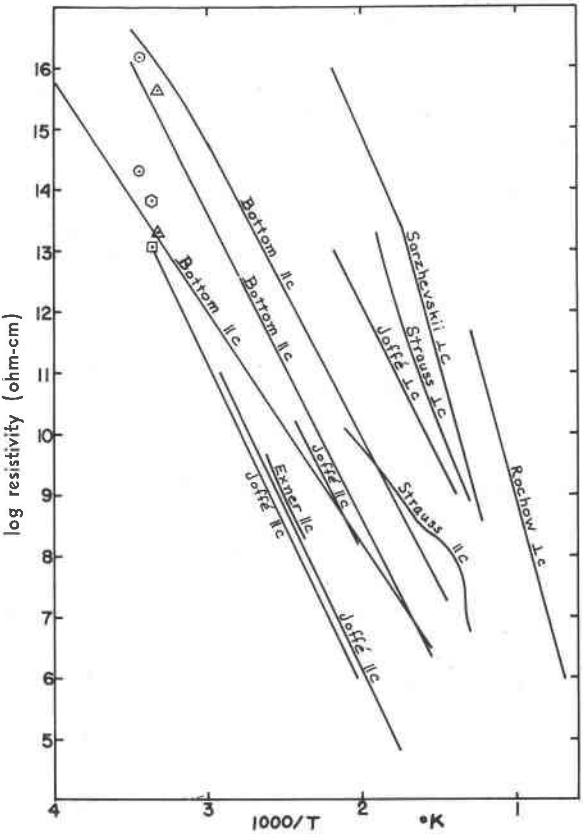

FIG. 1. Summary of published resistivity data, 1901–1956. Measurements over a range of temperature plotted as log resistivity vs. reciprocal of absolute temperature. Measurements at a single temperature by Thornton (circles), Curtis (hexagon), Richardson (triangles) and Klarmann (square).

techniques of the highest precision for their certain detection. Chemical analyses made in the course of that study revealed very low total impurity content (Table 3) and left considerable uncertainty as to the proper correlation of observed variations in physical properties with the impurities detected by analysis. Prof. C. S. Hurlbut suggested to the author in the fall of 1953 that light might be shed on these problems by the diffusion into quartz of impurity ions. Exploratory experiments yielded positive results, and a program to study the effects on the properties of quartz of impurity ions introduced by ionic diffusion was initiated.

In the course of this work precise information on the direct current resistivity of natural quartz became necessary in order to evaluate the contribution to the total conductivity of the introduced impurity ions undergoing diffusion. The data available in the literature presented a picture of inconsistency and contradiction quite at variance with the remarkable constancy of most of the other properties of quartz. Figure 1 summarizes the existing information up to the time of the present investigation. It will be noted that the values of axial resistivity* reported by different authors for any given temperature range over two decades. The slopes of the curves likewise show a wide range, indicating lack of agreement as to the energy of activation of the mechanism of conduction. As a result of the variation in slope of the curves, room temperature resistivities obtained by extrapolation (Table 1) show very large discrepancies. The agreement concerning the equatorial resistivity is only slightly better.

TABLE 1. SUMMARY OF EXPERIMENTAL METHODS

Author	Date	Temp (° C.)	Time of passage of current	Field intensity (volts/cm)	Electrode material	Resistivity (25° C.) (ohm-cm)	
						Axial	Equat.
Curie	1886–89	7–300	10s–11d	1–6000	Pt	1×10^{14}	3×10^{16}
Exner	1901	100–150	—	270–600	Na amalgam	1×10^{15}*	—
Thornton	1910	17	1m–144d	0.09–0.75†	none	2×10^{14}	1.5×10^{16}
Curtis	1912	26.5	0.5–1.0s	—	metallic	6.9×10^{13}	—
Richardson	1915–25	26.5	10s–20m	—	silver	2×10^{13}	4.3×10^{15}
Joffé	1928	26–500	to 190h	to 10,000	metal or graphite	1×10^{18}*	1×10^{19}*
Rochow	1938	500–1200	—	25	Pt foil	—	1×10^{29}*
Klarmann	1938	room	—	$1–2\times10^{5}$	silver	1.2×10^{13}	—
Sarzhevskii	1952	300–500	—	28000	—	—	$1\times1C^{2}$ *
Verhoogen	1952	300–500	to 10d	350–1750	Pt	1×10^{20}*	—
Bottom	1953	−42–416	15 m	—	aluminum	6.4×10^{13} 1.6×10^{16}	—
King	1955–56	85–462	to 600h	500	Pt	1×10^{26}* 1×10^{28}*	—
Strauss	1956	200–500	1–20m	1000(?)	stainless steel	1×10^{17}*	1×10^{23}*
Wenden	1955–57	25–535	to 1400h	to 2000	Pt	1×10^{27}*	

* Extrapolated value, given as an order of magnitude.
† e.s.u.

Differences between axial and equatorial resistivity reported by any one author are as great as 10^6, if curves are extrapolated to room temperature. Moreover, if the least value for axial resistivity is compared with the largest value for equatorial resistivity, both reduced to room temperature, the difference is greater than 10^{15}. There is no basis in theory for such enormous differences in axial and equatorial resistivity of pure, ordered quartz. It is very probable that this effect is dependent upon impurities, and indeed it was suggested as early as 1887 (Warburg and Tegetmeier) that the migration of sodium through quartz in the direc-

---

* "Axial resistivity" is considered to be the resistivity of a quartz crystal for current flowing parallel to the c axis.

tion of the c axis might account for the large observed difference in axial and equatorial resistivity. This is a reasonable postulate, and indicates that the resistivity is extraordinarily sensitive to impurity content, and hence is of peculiar significance in the study of the effect of such ions on the properties of quartz. For this reason, as well as to obtain reliable numerical values for this property, a series of careful measurements of the direct current resistivity were undertaken. This paper is a report on this phase of the problem.

Historical Note

The first significant measurements of the direct current resistivity of quartz were made by Jacques Curie as a part of a thesis on the electrical properties of crystals, and were reported in 1886, 1888 and 1889. At the same time research on the electrical resistivity of quartz was being carried out by Warburg and Tegetmeier (1887, 1888). These pioneer efforts were remarkably successful, and most of the important features of the direct current conductivitiy of quartz were clearly indicated. For example, Curie recognized the dependence of the resistivity on the time of passage of current, and made a quantitative statement of the current-time relation in exponential form. Likewise, Warburg and Tegetmeier clearly demonstrated the axial transport of charge by sodium ions through quartz plates, and correctly inferred that the greater part of the short-term conduction is electrolytic. However, these observations, valid in themselves, did not lead to correct inferences concerning the general mechanism of conduction in quartz, and the subsequent history of investigation of this property is one of disagreement and inconsistency, arising in the main from neglect by the experimenters of the factor of time of passage of current.

Experimental Methods

The block diagram (Fig. 2) shows the essential elements of the apparatus used in the present study. Figure 4 shows the layout of the equipment and identifies the components.

A Z-cut disc of optical grade Brazilian quartz, polished on both surfaces, is placed in a vertical muffle furnace between platinum foil electrodes, and upon the upper electrode, insulated from it by a one-inch quartz cylinder, are placed stainless steel weights to maintain good contact. Another quartz cylinder insulates the lower electrode from the stainless steel block on which it rests, and the self-supporting leads from the electrodes leave the furnace through oversize clearance holes in the ceramic base. Figure 3 shows the holder assembly and furnace construction. A regulated power supply furnishing 0–1500 volts in 150 volt steps is connected in series with the test sample and the decade shunt of a

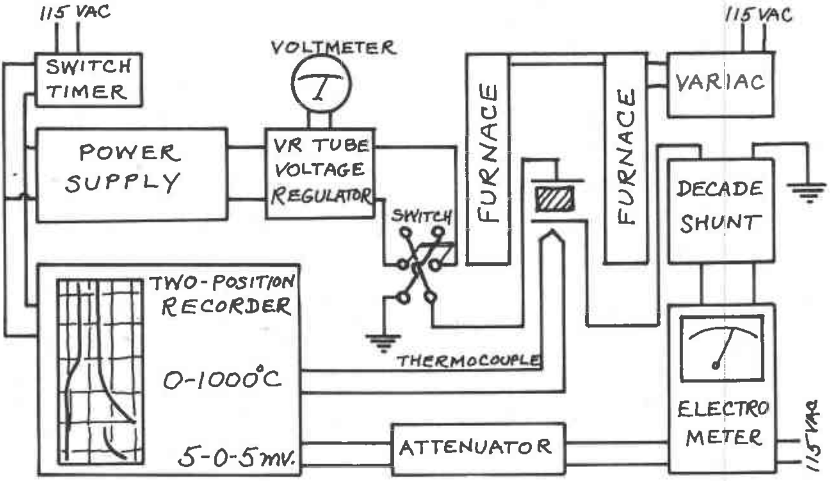

FIG. 2. Block diagram of apparatus for resistivity measurement.

Keithley Model 210 electrometer. A potential is impressed across the sample and a current flows through the shunt. The voltage across the shunt is read by the electrometer, whose output drives the 0–5 millivolt range of a two-position Leeds-Northrop Model G Speedomax recorder through a suitable attenuator. A thermocouple in the stainless steel block beneath the sample holder actuates the second range of the Speedomax recorder, which is directly calibrated in degrees C., so that a continuous record of furnace temperature and current flowing in the plate under test are kept on the same strip chart. A switch permits reversal of polarity of the applied voltage.

The furnace is counterweighted and slides up and down easily on stainless steel rods. The support framework of the furnace is designed to accommodate the electrometer beneath the furnace so that the critical lead from the sample to the high side of the electrometer shunt may be kept short. Furnace temperature is set by means of a General Radio V5 Variac, and line voltage fluctuations are suppressed by use of Raytheon voltage stabilizers.

The overall precision of the measurements is low, plus or minus 10 per cent, but is adequate for the purposes of this investigation. The general accuracy of the instruments was checked at regular intervals by comparison of the reading of the Speedomax against two different portable potentiometers, and by calibration of the voltage scales of the electrometer against standard cells. No guard electrode was used, as Rochow (1938) and others have shown that the error resulting from surface conduction is negligible above about 200° C.

Study of the ionic conductivity of quartz and of the mobility of ions

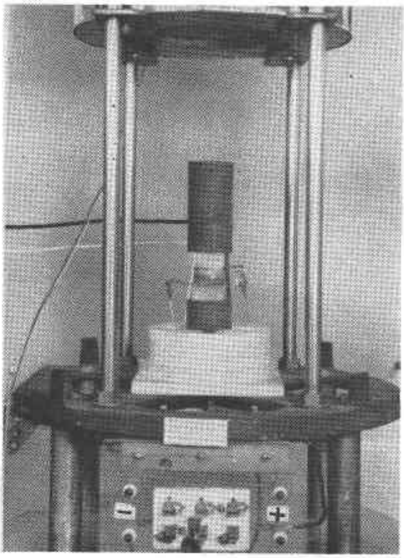

FIG. 3. Sample holder arrangement and furnace construction. Polarity reversing switch at lower center.

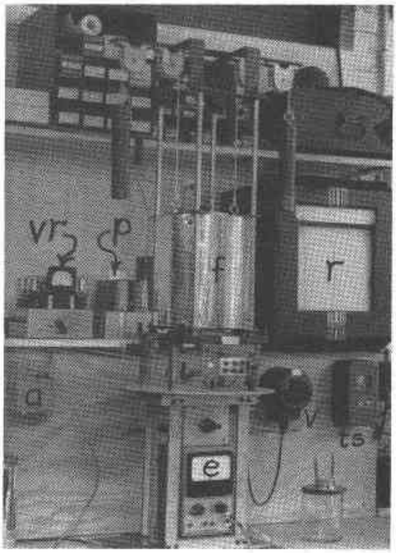

FIG. 4. Resistivity apparatus. *a*, attenuator; *e*, electrometer; *f*, furnace; *r*, recorder; *p*, power supply; *vr*, voltage regulator; *v*, variac; *ts*, time switch.

in quartz may be carried out simply by inserting between the quartz plate and the platinum anode a pressed pellet of a non-volatile, non-hygroscopic salt of the ion of interest. In Fig. 3, such a pellet of sodium chloride may be seen in place above the quartz disc. Ionic diffusion aspects of this study will be discussed in a later publication.

DEPENDENCE OF THE RESISTIVITY ON TIME OF PASSAGE OF CURRENT

Of the many factors which determine the resistivity of quartz, the length of time during which the current flows in the sample is that which produces the largest effect, and which has the most complex relationship with the numerical value of the resistivity. For example, passage of current through a plate of quartz for over 500 hours produced an increase in resistivity of 10^8 ohm-cm.

Whenever a potential is applied to a plate of quartz a current flows which is large at first and diminishes rapidly with time. This current consists of four parts, each of which has its own time dependence. These are, in the order of their appearance:

(*a*) the normal dielectric charging current
(*b*) the anomalous charging current
(*c*) the surge current
(*d*) the steady-state direct conduction current

(*a*) The normal dielectric charging current, or displacement current, appears as an instantaneous "kick" of the galvanometer as the capacitor formed by the platinum electrodes, leads and switch gear charges. This current is generally interpreted as displacement in an applied electric field either of electrons in the electronic superstructure of ions, or of cations and anions relative to each other in the structure. The relative importance of the two types of displacement depends on the frequency of the exciting field (Mott and Gurney (1948)). In direct current measurements, where the capacitance of the circuit yields a time constant of a fraction of a second, this mechanism is of no practical importance.

(*b*) The anomalous currents are small currents which make their appearance whenever potential is changed, a charging current if the potential is increased, a discharging current if the potential is decreased. These currents are of short duration, having a relaxation time of the order of minutes, and are superposed on the currents resulting from other modes of conduction. Hence, when the currents due to other modes of conduction are very small the anomalous currents form a significant part of the total current, and the Law of Superposition, as stated by Curie (1889) and generalized by Jacquerod and Mugeli (1922) holds. This law may be stated: "The total quantity of electricity transported by the anomalous charging current is equal to that transported by the anomalous discharge current." This may be stated:

$$Q_{\text{charging}} = \int_0^t \mathrm{I}_c dt = Q_{\text{discharging}} = \int_t^\infty \mathrm{I}_d dt$$

Q is the quantity of charge in coulombs, I_c and I_d are the charging and discharging currents in amperes, respectively, t is time in seconds, and if it is supposed that the circuit is closed at time 0, charging current flows until time t, upon which the potential is removed or shorted out, and discharge current then flows until time ∞. Essentially complete charge and discharge, as measured with a practical electrometer, is reached in 5–15 minutes.

In an effort to isolate the mechanism of conduction responsible for the anomalous charging and discharging currents some experiments were undertaken using manually switched square-wave alternating current at frequencies of 1/900, 1/300 and 1/60 cycles per second.

At the time these experiments were made current had flowed in the test plate for a total of 108 hours at elevated temperature, so that further decrease of current during the short period of the tests was negligible. The tests were made at 100° C., a temperature at which the direct conduction current was too small to measure on the Keithley electrometer.

Polarity was reversed every 15 minutes, 5 minutes and 1 minute in

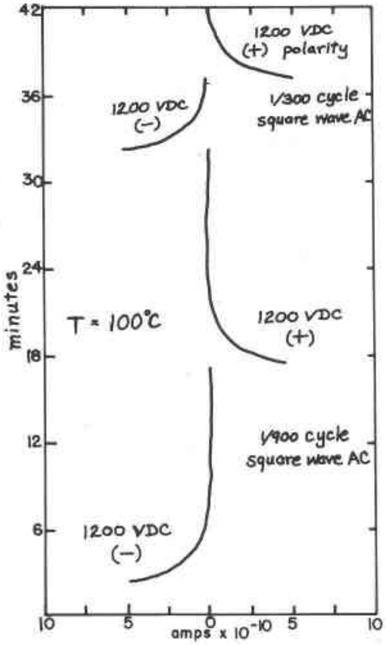

FIG. 5. Current-time curves for square wave alternating current at 100° C. Traced directly from the Speedomax strip chart.

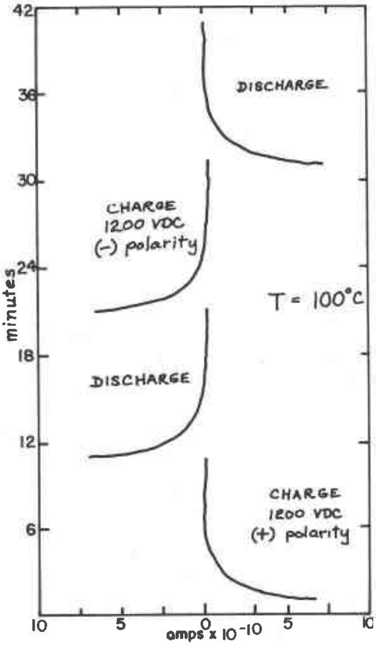

FIG. 6. Current-time curves for anomalous charging and discharging currents at 100° C. Traced directly from the Speedomax strip chart.

succession, recording several cycles at each frequency. Figure 5 is a tracing of the strip chart record for the 1/900 and 1/300 cycle/sec frequencies. Each half cycle is entirely symmetrical with the half cycles preceding and following. The mode of current decay for each half cycle can be closely approximated by Curie's formula

$$\rho = At^n \quad \text{where} \quad \left.\begin{aligned} A &= 10^{12} \\ n &= 1.4 \end{aligned}\right\} \text{ at } 100^\circ \text{ C.}$$

and ρ is resistivity in ohm-cm, t is time in seconds, and A and n are constants for a given temperature.

Hence, although there is, strictly speaking, no measurable direct current flowing, if the time t above is small compared to the relaxation time of 6–7 minutes observed, there will be an alternating current flow that is appreciable due entirely to the anomalous charging current. In this way, the anomalous phenomenon acts to store and return energy into the external circuit just as a capacitor does. The question may arise, is this not in fact a capacitative effect? The capacitance of the platinum electrodes may be computed from the formula for a parallel plate capacitor as 0.7 $\mu\mu fd$ with air dielectric ($K=1$) for one inch diameter electrodes spaced 0.25 inch apart. But the capacitance of the system required to yield the charging current curve observed may be found from the formula

$$C = \frac{t}{R \log_e (E_0/E_t)} \text{ farads}$$

where t is time in seconds, E_0 the initial voltage read on the electrometer across shunting resistor R, and E_t the voltage read at time t. This formula is valid for capacitors either charging or discharging through a resistor, in this case the entire capacitance of the system discharging through the shunt in the decade box, 10^{10} ohms. Solving,

$$C = \frac{120}{10^{10} \log_e (5.2/1.5)} = 9650 \ \mu\mu fd$$

This capacitance requires a dielectric constant for quartz of 13786. Whereas this is not an impossible value for dielectric constant, it is larger by a factor of 3000 than the customary value of 4.6 for the axial dielectric constant of quartz. Furthermore, if similar measurements are made at higher temperature, the value of K required becomes even greater. However, for alternating currents having higher frequencies, over 0.1 cycle /sec, the mechanism considered here does not operate, as the rise time of this current is of the order of a few seconds.

Joffé (1928) discards the concept of a change of dielectric constant of this magnitude as implying viscous processes in crystals for which no evidence exists. Field (1944), following Maxwell's theory of layered dielectrics, suggests that such an increase in dielectric constant results from the accumulation of charge carriers, either ions or electrons, at domain interfaces and submicroscopic defects in the lattice, constituting a reversible polarization which he terms interfacial polarization.

Field (1944) points out that if we consider the dielectric constant for optical frequencies, which is equal to the square of the index of refraction, as the result of electronic polarization and come down the scale of frequency, each new type of polarization encountered will produce an increase in the dielectric constant. Each type of polarization has associated with it a relaxation time T at which the polarization is within $1/e$ of completion, and a relaxation frequency f_m connected with the relaxation time T by the equation

$$f_m = \frac{1}{2\pi T}$$

at which frequency the loss factor has a maximum value. Entering this equation with values of T derived from the experiments described we find values for f_m in the range 0.01–0.001 cycle for the anomalous currents.

In the case of quartz, the mean dielectric constant for optical frequencies is about 2.4. For radio frequencies, the mean dielectric constant is about 4.6 for all frequencies from power to UHF. Hence, a relaxation frequency must lie somewhere in the microwave-infrared region, associated with the excitation of a new type of polarization, probably ionic displacement of lattice ions. We have just seen that there is evidence for another increase in dielectric constant in the 0.01–0.001 cycle/sec region. This increase must reflect the appearance of still another type of polarization. Field (1944) and Murphy and Morgan (1937) consider this to be interfacial polarization in the case of various commercial ceramic dielectric materials. Figure 7 shows the behavior of the dielectric constant and loss factor of quartz with frequency.

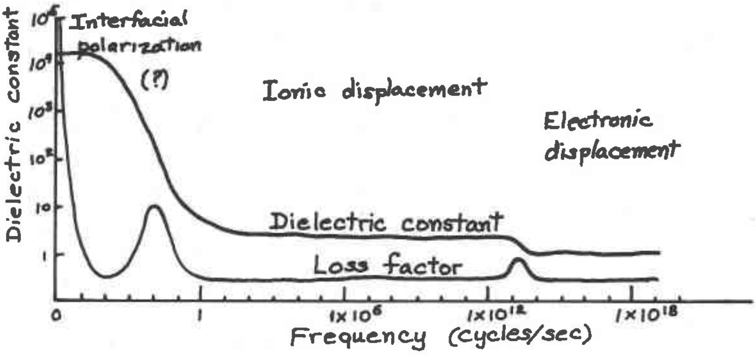

FIG. 7. Dielectric constant and loss factor of quartz over a wide range of frequency.

A series of charging and discharging curves were also recorded at 100° C. (Fig. 6) by applying a potential for 10 minutes, short circuiting the power supply for 10 minutes, applying potential with reversed polarity for 10 minutes, then shorting the power source for another 10 minutes. Charge and discharge curves are identical within the limits of precision of the method, indicating that the Law of Superposition holds, and that the phenomenon is completely reversible. The relation

$$Q_{\text{charging}} = Q_{\text{discharging}}$$

holds, and no direct current flow has taken place.

When this experiment is repeated at a higher temperature, the Law of Superposition holds for the anomalous part of the current, but does not for the entire observed current because the direct conduction current is large compared with the anomalous current. For this reason, charging and discharging curves taken at 280° C. are not symmetrical nor identical. In Fig. 8 note that the scales for charge and discharge currents are not the same. The discharge current for either polarity is identical in

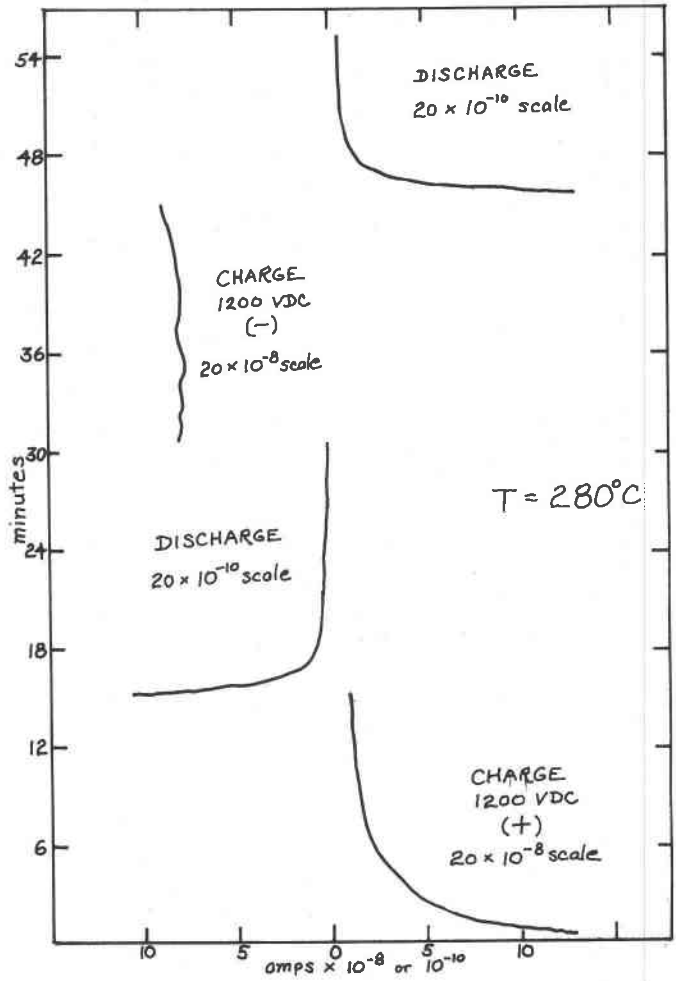

FIG. 8. Current-time curves showing charging and discharging current at 280° C. Note that the scale for the charging current is not the same as that for the discharging current. Traced directly from the Speedomax strip chart.

magnitude and waveform to that yielded after charging with opposite polarity at the same temperature for the same time, although the charging current curves display an asymmetry resulting from the semiconductor behavior of quartz discussed later in this paper.

This experiment indicates clearly that the anomalous charging currents are independent of, and superposed on those currents carried by other mechanisms. The anomalous currents increase with increase in temperature, but at a much smaller rate than the direct conduction current. When the temperature was increased from 100° C. to 280° C. in the preceding experiment, the increase in peak value of charging current was only about 0.3 per cent of the increase in direct conduction current. Thus, the anomalous currents seem to be present at all temperatures but relatively insensitive to temperature changes. They probably contribute little to the net conduction. They are not a significant source of error in measurements of resistivity unless the current is read within a few minutes after application of potential. We may consider that these currents are caused by displacement of non-lattice ionic and possible electronic charge carriers, and that the decay of the charging current is the result of the reversible trapping of charge carriers at domain interfaces and lattice imperfections. The discharge current is the result of equalization of distribution of charges after the removal of the exciting potential. Sarzhevskii (1952) has shown that free electrons exist in quartz at temperatures below 300° C. and these may play a part in the anomalous currents at these temperatures, but the dominant role of cations seems to be established by Joffé's (1928) observation that the density of the space charges which appear in quartz in an electric field is always greatest near the cathode, regardless of polarity.

(*c*) The third part of the current is one which constitutes the largest part of the total current for several hours after application of potential, and which because of its behavior I shall call surge current. Upon application of *e.m.f.* for the first time at any given temperature, current rises rapidly to a maximum, reaching peak value in less than three minutes, and in many cases in less than one second. Thereafter, current decreases with passage of time.

The decrease is rapid for the first hour, generally to one per cent or less of the initial peak current. For the next 5–7 hours the current decays less rapidly, reaching about 50 per cent of the one hour current at 6–8 hours from the start of the run. The current then falls much more slowly, the rate of change of current with time decreasing slowly as current decreases. This trend continues for over 500 hours.

For time of flow of current up to one hour, the rate of decay of current, ratio of peak current to one hour current, and form of the decay curve differ from run to run, temperature to temperature, and sample to sample (Fig. 9). However, after the first hour, a pattern is well established. From about the end of the first hour to the sixth or eighth hour, if the logarithm of the resistivity is plotted against the reciprocal of the time, this portion of the curve is almost a straight line (Fig. 10). About the sixth to the eighth hour, a fairly sharp inflection in the log reciprocal curve indicates a decrease in rate of change of current with time. Beyond 24 hours, the curve becomes asymptotic.

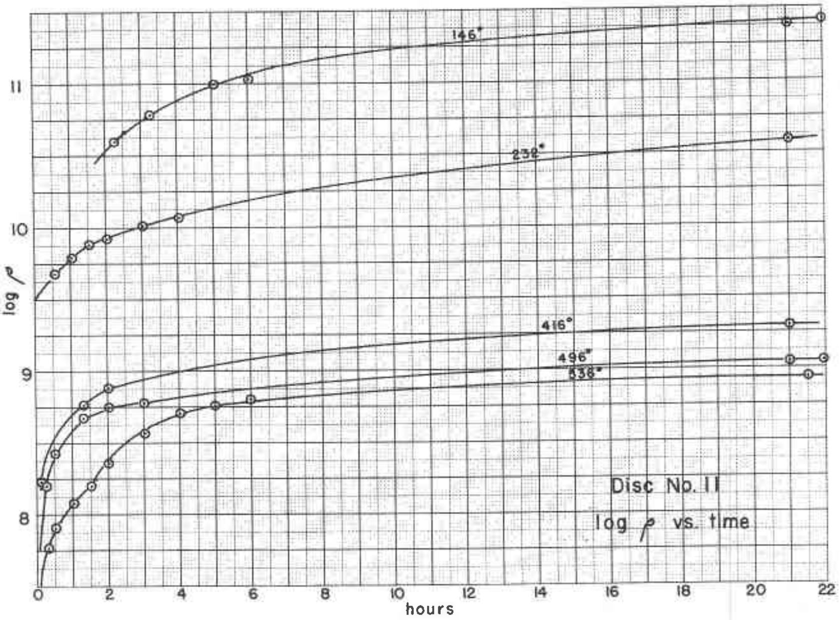

FIG. 9. Logarithm of resistivity in ohm-cm. vs. time in hours.

Thus, the resistivity-time relation may be divided into three fairly distinct phases:

(1) rapid and rather erratic increase in resistivity during the first hour
(2) more gradual increase in resistivity approximating to an exponential function of time from one hour to 6–8 hours
(3) still slower increase of resistivity from 6–8 hours to over 500 hours, becoming negligible

This threefold division of the current-time relation was observed also by Thornton (1910) using a wholly different method of experimentation. Note that this threefold division does not include the anomalous current. The surge current is, for temperatures above 200° C. during the time that it is dominant, orders of magnitude greater than the anomalous current. The surge current has a very marked temperature dependence, leading to activation energies in the range 10–30 kcal/mole, whereas the anomalous currents increase only slightly with temperature. The polarization causing the anomalous currents is completely reversible, whereas the mechanism causing the surge current is almost completely irreversible.

It is of interest to note that Curie (1889) stated the relation between resistivity and time in the form

$$\rho = aT^n$$

where ρ is the resistivity, T is the time, a and n are constants, a depending chiefly on temperature, and n roughly constant for a given specimen.

This equation was tested and found to fit reasonably well that portion of the time-resistivity curve between one and eight hours. The generalization fails for longer runs, and Curie's constants a and n for runs which exceeded one day are markedly different from those for runs of three hours or less. The decay curve of the anomalous current has the same general form, a circumstance which has probably given rise to a great many misunderstandings. Most authors fail to distinguish between the surge current and the anomalous current on the one hand, or between the surge current and the steady-state conduction current on the other. The surge current is a transitory, but perfectly definite phase of the conduction process in dielectrics. The empirical data accumulated during the present study concerning the surge currents can be fitted only by an expression containing additive terms, which may themselves be complex functions. An example of such a general expression is that derived by Jacquerod and Mugeli (1922) for the anomalous resistivity, and has the form

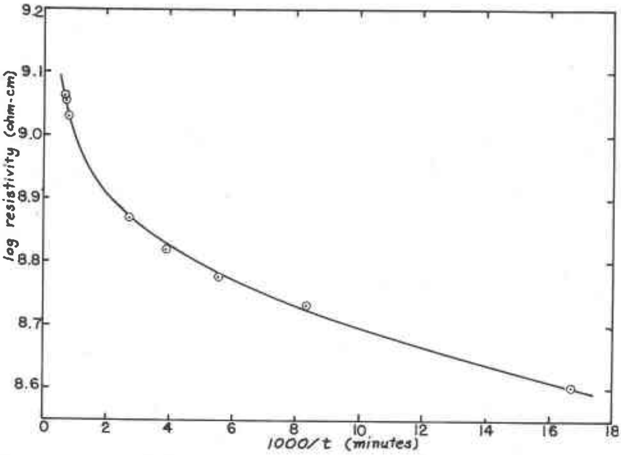

FIG. 10. Log resistivity vs. reciprocal of time in minutes. Disc No. 11 at 499° C.

$$\rho = \rho_0 e^{at} + \rho_1 e^{bt} + \rho_2 e^{ct}$$

where ρ_0, ρ_1, and ρ_2; a, b, and c are constants.

If, after the passage of current in a given direction and at a fixed temperature for 24 hours, the polarity is suddenly reversed, the resistivity-time relation for the new polarity is not symmetrical with the first run. Repeated reversals of polarity produce runs adhering to the same pattern. The maxima of current are always higher for the runs whose polarity corresponds with that first selected, and the time of rise to maximum is shorter, whereas for all subsequent runs on the opposite polarity, alternating with those of the first polarity, the maxima are lower and the rise times longer. In all cases, after less than four hours, these initial effects have disappeared and current declines slowly, the absolute value depending only on the total time elapsed since the beginning of the first run, and not on polarity or sequence of polarity changes. Table 2 gives current and time values for two temperatures.

TABLE 2. POLARITY SENSITIVE EFFECTS IN ELECTRICAL CONDUCTION IN QUARTZ

Temp (° C.)	Run	Polarity	Maximum current (amps)	Rise time (mins)	24-hour current (amps)
418	1	+	3.7×10^{-3}	1	5.0×10^{-6}
	2	−	3.1×10^{-4}	18	3.8×10^{-6}
	3	+	8.3×10^{-4}	10	3.2×10^{-6}
	4	−	2.0×10^{-4}	26	2.5×10^{-6}
499	1	+	4.1×10^{-3}	2	8.3×10^{-6}
	2	−	2.8×10^{-4}	17	7.8×10^{-6}
	3	+	1.0×10^{-3}	6	6.3×10^{-6}
	4	−	2.5×10^{-4}	20	5.2×10^{-6}

This simply means that quartz, for the short-term surge current, behaves as a semiconductor, in which the first application of potential determines the polarity of the forward, or easy, direction of conduction, so that the magnitude of the current flowing at any time thereafter depends not only on the potential and the temperature, but also on the direction of flow.

Up to the current maximum and for a few hours thereafter the dominant mechanism of conduction is one whose activation energy is low and varies from sample to sample. While this mechanism dominates, the sample may show semiconductor characteristics. After the disappearance in 4–8 hours of polarity sensitive effects, the conduction is dominated by a mechanism of higher energy of activation which operates progressively, so that current becomes a function only of total time of passage of current for a given temperature and potential.

This large initial current, the surge current, is almost certainly attributable to the mobilization of non-lattice impurity ions acting as charge carriers. These may, upon continued maintenance of an electric field, become irreversibly trapped in lattice defects or migrate to the surface of the test sample and there plate out, so as to become unavailable for further transfer of charges. At any given temperature, the trapping and exclusion of ionic carriers at the surface of the plate or in lattice defects during the initial current surge introduces a polarity-sensitive or semiconductor behavior apparent in all later runs at that temperature. The carriers involved in this mechanism are those impurity ions most favorably placed to participate immediately in conduction with a low energy of activation. As these become exhausted by irreversible trapping or removal, the initial surge current decays, giving way to the more slowly decreasing current (long-term surge current) carried by interstitial impurity ions less favorably placed for conduction. These latter ions probably move through the celebrated "tunnels" or "pores" parallel to the c axis, whereas the ions contributing to the early surge current may be located along domain boundaries, growth lines or other imperfections and hence are less firmly bound.

The reality of this process of exclusion and plating out of impurity ions is attested by the visible deposit of salts found at the cathode surface of every plate of natural quartz that underwent a long resistivity run. Although too scanty for analysis, these cathode deposits yield a qualitative test for sodium, and Verhoogen (1952) describes the collection of detectable amounts of boron at the cathode after measurement of an Arizona quartz crystal. If such a plate is cleaned and rerun at a later time, the resistivity remains high and surge current effects are much less marked than during the first run.

(*d*) The fourth part of the current is the long-term, steady-state current which becomes manifest only after the disappearance of the short-term effects. Decay of the masking impurity ion currents seems to be complete at 1200 hours, and may in some cases, be complete at 500.

Mott and Gurney (1948) suggest that this current may be due, at the higher temperatures, to mobilization of all the ions in a crystal, or all the ions of one sign. Demonstration of the electrolysis of quartz is difficult, since the total amount of silicon that would be liberated by a current of 10×10^{-6} amperes is

$$m = \frac{It(7.01)}{96,485} = 6.3 \times 10^{-5} \text{ gms./day}$$

Slightly more than half as much oxygen would be produced. At the rate computed more than three months would be required to accumulate 6 mg. of silicon at the cathode. The current postulated above is approximately that which would flow through a one-quarter inch plate of quartz at a potential of 1500 volts during a lengthy run. Electrolytic dissociation of the quartz could certainly account for the observed currents without visible deterioration of the plate. It may well be, however, that only oxygen ions, or oxygen ions and holes, are mobile.

Sarzhevskii (1952) has shown by the absence of the Hall magnetoresistance effect above 300° C. that the conductivity is primarily ionic above that temperature. The number of free conduction electrons below 300° C., where a Hall effect was noted, is 10 to 10^5 electrons/cm^3. This small number indicates that the conductivity of quartz at all temperatures is predominantly ionic. Sarzhevskii's work was done on equatorial plates, and consequently the conductivity he discusses is chiefly the characteristic, or steady-state, conductivity, since short-term surge current effects are much less marked in equatorial plates.

The question of the ability of impurity ions to carry the current observed to flow up to the point where the steady-state mechanism becomes dominant may be settled by reference to analyses of quartz made during a Harvard study (Frondel and Hurlbut (1953)) which are presented in Table 3.

Table 3. Analyses of Quartz (Weight Per Cent)

Sample	Ti	Mn	Fe	Al_2O_3	Na	K	Li
1	0.0001	0.00002	—	0.0008	0.0004	0.0002	0.0005
2	.0002	.00002	.0003	.0008	—	—	.0004

1. Colorless quartz (C105), Arkansas.
2. Dark smoky quartz (S101), Brazil.

These analyses are taken as representative of clear quartz, and hence of the optical grade material used in this study. Total impurities do not, in general, exceed 0.1 per cent, even in strongly colored and visibly impure material. Calculating on the basis that all ions except aluminum, which is considered to be in tetrahedral coordination, are mobile and free to participate in conduction, the impurities listed for Sample Number 1 in Table 3 are capable of transferring 0.638 coulombs of charge. In terms of a typical current-time curve, such as that shown for 496° C. in Fig. 9, this means that the impurity ions are capable of carrying the total integrated current up to 10.5 hours from the beginning of the run. Since the steady-state mechanism is also participating, the effects consequent upon the presence of impurities may be expected to die away in 12–24 hours, a figure in good agreement as to order of magnitude with suppositions based on the nature of current decay and the disappearance of semiconductor effects. At the end of this time, the current must be carried entirely by the steady-state mechanism. If the temperature is raised, a new current surge is to be expected, since ions irreversibly trapped at the lower temperature may be freed to participate in the short-term conduction again at a higher temperature.

Even if we assume a figure for the total mobile impurities ten times greater than that given by analyses 1 and 2, the capacity of these impurity ions to transfer charges could still be exhausted within the duration of the runs made in this study. Since Sarzhevskii's work seems to indicate that this current cannot be electronic, we are forced to the conclusion that the long term, steady-state current must arise from electrolysis of the quartz itself.

VARIATION OF RESISTIVITY WITH TEMPERATURE

Perhaps the most fruitful approach to the mechanism of conduction in quartz is through variation of resistivity with temperature. In this study, the upper limit of temperature was arbitrarily set at about 540° C. The resistivity of high quartz was not considered. The lower limit was set by the sensitivity of the electrometer at about 25° C.

The chief problem in studying the variation of resistivity with temperature is the separation of the effects of temperature from the effects of elapsed time and applied potential.

Some experimenters have used alternating current, which involves a frequency-sensitive polarization and yields small values for the resistivity compared with direct current measurements made over long periods of time. Other experimenters have used direct current, but have applied potential at a given temperature for only short periods, reversing polarity after a few minutes, and taking the average of the readings made on opposite polarities as the current for that temperature. The potential is then removed while the plate is brought to a new temperature. In this way an entire sequence of measurements over a wide temperature range may be made without exceeding a few hours total time of passage of current. Thus, all measurements are made within the period of dominance of the short-term surge current. If readings are taken after 15 minutes or more, the anomalous current is excluded; if after a shorter time interval, a portion of this current is also included. If a regular procedure is followed at all temperatures, a self-consistent body of data may be obtained, yielding the activation energy for the short term mechanism. This seems to have been the procedure followed by most early investigators. Disc No. 12 (Fig. 12) was measured in this way and yields, for the resistivity, good agreement with the mean of Bottom's (1953) results, (Fig. 1) and for the activation energy, good agreement with the mean of all earlier investigators for axial resistivity. Measurements made in this way plot as straight lines on the conventional arith-log display of log resistivity vs. reciprocal of absolute temperature, provided all measurements were made the same length of time after application of potential.

Investigators differed widely in their practice as to time of reading current after application of potential. Curie (1889) recommended one minute, F. Braun suggested 24 hours. Others have attempted to read instantaneous peak current at the moment of application of potential. Strauss (1955) read current every minute, reversing polarity every 20 minutes, while increasing temperature uniformly. Other investigators maintain potential at all times and cycle temperature, reading current whenever thermal equilibrium is established. Unless current is first allowed to pass through the test plate for a period of hundreds of hours, measurements of this kind result in an inextricable mingling of the effects of temperature and time. Such measurements plot on the log resistivity vs. reciprocal temperature graph as curved rather than straight lines.

The principal reason for the diversity of results and lack of agreement among these investigators lies in the different methods of dealing with the factor of time.

In order to separate the effects of temperature and time it is necessary to allow current to pass through the plate until further changes of current with time are negligible. The temperature may then be cycled with potential continuously applied, and measurements of current made whenever thermal equilibrium is reached. A total of 70 current measurements was made on one such plate (Disc No. 11) through which current had been passed for over 500 hours.

A plot of these 70 points (Fig. 11) reveals two straight line segments joined at an inflection point at about 350° C. This test plate, through which current had been passed with positive polarity for nearly 600 hours, was removed from the furnace for about four weeks. It was then thoroughly cleaned and reassembled in the furnace with clean platinum electrodes. A new series of measurements was then made with negative polarity from 26° C. to 525° C. The values of resistivity obtained were in close agreement with the earlier values, but were slightly higher. A final series of measurements were taken on this plate after the total cumulative time reached 1400 hours (Fig. 11). This series is best represented as a straight line without inflections on the log resistivity-reciprocal temperature plot.

The overall tendency in this last experiment was to straighten out the resistivity temperature curve, and increase all values of resistivity. This indicates that quartz which has been electrically treated does not regain its initial conductivity by standing for a time comparable with the time of passage of current, as claimed by Curie (1889). Both high and low temperature portions of this curve move toward higher resistivity with time. The low temperature branch changes somewhat in slope with passage of time and the inflection appears to migrate to lower temperatures, finally disappearing, whereas the high temperature portion moves more nearly parallel to itself.

The work of King (1955, 1956) has strikingly confirmed these findings. In King's experiments the factor of time has been effectively separated from that of temperature, following Wenden (1955), by passing current through the plate for a period of weeks before making measurements. Accordingly, his results are directly comparable with those reported here, and afford excellent numerical agreement both as to absolute resistivity and activation energy (Fig. 12 and Table 5). Since King's observations embody some at temperatures lower than were possible with the Keithley electrometer, they extend the results of this study in a most interesting way. It appears that the knee, or inflection point of the two-branched curve described above does not disappear with continued passage of current, but migrates to lower and lower temperatures. Hence, we may conceive of a family of curves resulting from a series of measurements of resistivity at different times during a very long run like those shown in Fig. 13.

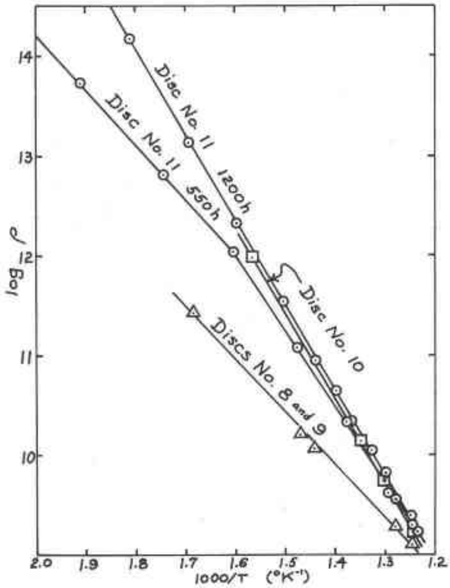

FIG. 11. Logarithm of resistivity vs. reciprocal of absolute temperature for Discs 8 and 9, 10, and Disc No. 11 after passage of current for 550 hours, and again after passage of current for 1200 hours. See Table 5a for identification of disc numbers. All are Z-cut discs of natural quartz.

Considering separately the two portions of the two-branched curve obtained after three weeks (Disc No. 11, Fig. 11), it is found that each may be represented within the limits of error of the method by an expression having the form

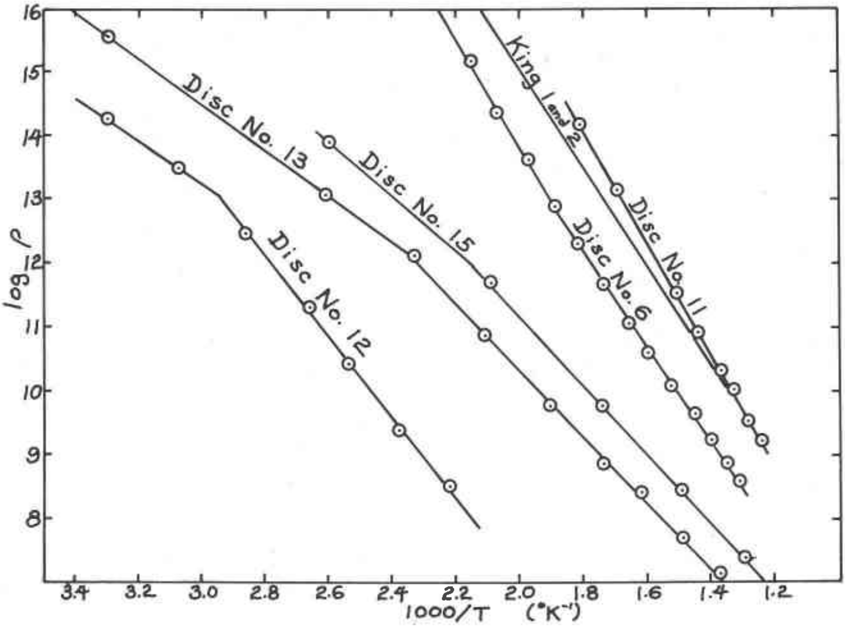

FIG. 12. Log resistivity vs. reciprocal temperature. Discs 11, 12 and 13 are Z-cut, Disc No. 6 is inclined 51°40′ and Disc No. 15 is X-cut. Discs No. 13 and 15 were run with NaCl anodes. Discs 11 and 6 passed current for 1400 and 2000 hours, Disc No. 12 for about 3½ hours. King's (1956) curve for natural quartz is included for comparison.

$$\rho_1 = A_1 e^{U_1/RT}$$

If T is given values lying between 298° and 623° K., ρ_1 is the resistivity over that range of temperature, U_1 is the activation energy of the dominant mechanism of conduction over that range, R is the molar gas constant equal approximately to 2.0, and A_1 is a constant which fixes the absolute values of resistivity. Similarly, for the upper branch of the curve

$$\rho_2 = A_2 e^{U_2/RT}$$

where the symbols have the same meaning as before except that T has values between 623° and 809° K., and ρ_2, U_2 and A_2 apply to this temperature range.

Calculation of the constants from the measured values of resistivity yield

Temperature Range	U	A
298°–623° K.	26.0 kcal./mole	910
623°–809° K.	34.0 kcal./mole	1.47

Calculation of the activation energy from the values of resistivity measured after passage of current for over eight weeks yields only one value, which affords a good fit for all observations recorded. The inflection point present in the earlier observations made on this same sample has migrated to lower temperature, beyond the range of sensitivity of the electrometer.

Temperature Range	*U*	*A*
279°–808° K.	39.5 kcal./mole	24.55

The activation energy *U* is notably higher, reflecting an increase in slope for the curve as a whole.

Many experimenters have found that similar expressions may be used to represent the conductivity of ionic crystals (Mott and Gurney (1948), pp. 36–63; Jost (1952), pp. 179–197). Two-branched curves, the higher temperature branch having the greater activation energy, have been observed in NaCl, LiCl, LiF, KBr and most of the other alkali halides, and also in PbI_2 and other salts of lead, silver and copper. These curves are represented by Smekal, Lehfeldt and Seith by formulas having the form

$$\sigma = A_1 e^{-U_1/RT} + A_2 e^{-U_2/RT}$$

consisting of additive terms of exponential form, where the symbols A, U, R, etc., have the same meaning as in the discussion immediately preceding, and σ is the conductivity.

Interpretation of these terms is varied. Smekal considers the first term (in NaCl) to correspond to conduction by surface particles, whereas the second represents electrolytic conduction in the normal lattice. Seith interprets the first term in PbI_2 as the conductivity of the Pb ions, and the second term as the conductivity due to the I ions. Jost suggests the first term may represent the influence of interstitial impurity ions, whereas the second term reflects the "correct conductivity" of the crystal. Mott and Gurney, in commenting on Smekal's results for NaCl, reject Smekal's interpretation of the first term as surface conductivity, and remark that (p. 39): "Clearly the first term gives the conductivity due to a small number of ions in special places, which can be released easily, while the second term is that due to a large number; all the ions in the crystal, or all the ions of one sign, which can only be released with greater difficulty." Mott and Gurney refer to the first term as the "structure-sensitive" part of the conductivity.

The calculated activation energy for the low temperature mechanism in Disc No. 11 above, and the activation energy for Disc No. 12, which was measured so as to obtain the activation energy of the short term mechanism, are both very close to that found for the diffusion of alkali metal ions in quartz (Tables 4 and 5). Table 5 shows, for purposes of comparison, the activation energies for conduction mechanisms in quartz.

There is, in the data presented in Tables 4 and 5, a very strong suggestion that all investigators prior to Wenden (1955) and King (1955, 1956) have been measuring, not the axial resistivity of quartz, but the mobility in quartz of impurity ions; from the activation energies reported, probably alkali metal ions.

Activation energies and absolute magnitudes both suggest that the equatorial resistivities of earlier workers were more nearly a measure of the actual resistivity of pure quartz, but the wide spread to be found in the published results, coupled with experimental evidence from this study (Fig. 12), indicate that ionic diffusion and lattice defects influence the equatorial resistivity as well. Compare curves for Discs 13 and 15.

VOLTAGE DEPENDENCE OF RESISTIVITY

It has long been recognized that quartz, like many other dielectrics, does not rigorously obey Ohm's Law. That is, the relation between voltage and current for a given temperature is not linear, and the apparent resistivity of a sample held at constant temperature varies with the intensity of the electric field applied to it (Fig. 13). Shaposhnikov (1910) stated that quartz obeys Ohm's Law up to a field intensity of 4000 volts /cm for short periods, with the resistivity decreasing for more intense fields or longer times of flow. Frenkel (1938) suggested for the relation of

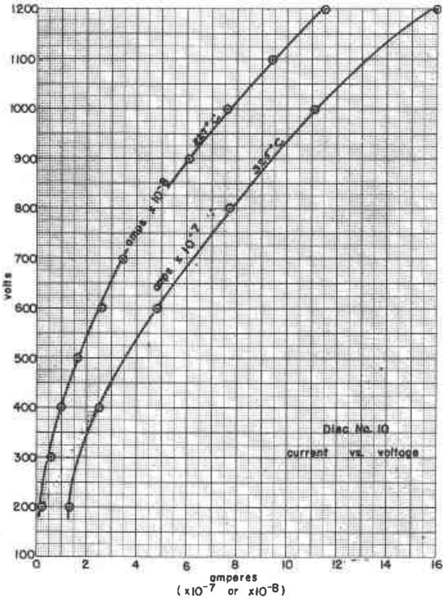

FIG. 13. Non-linear relation between voltage and current for quartz.

TABLE 4. ACTIVATION ENERGIES OF ALKALI METAL IONS IN QUARTZ

Ion	Activation energy	Author	Date
Li	20.4 kcal./mole	Verhoogen	1952
Li	17.7 kcal./mole	Stuart	1955
Na	22–25 kcal./mole	Vogel & Gibson	1950
Na	24 kcal./mole	Verhoogen	1952
Na	24.1 kcal./mole	Wenden	1957
K	31.7 kcal./mole	Verhoogen	1952

resistivity to field intensity the expression

$$\rho = \rho_0 e^{-\beta\sqrt{E}}$$

where ρ_0 is a constant determining the absolute magnitude of the resistivity and β is a constant depending on the orientation of the sample. E is the field intensity in volts/cm.

Sarzhevskii (1952) incorporated Frenkel's formula into a two-term expression for the dependence of resistivity on both temperature and voltage

$$\rho = \rho_1 e^{B_1/T} + \rho_2 e^{B_2/T}$$

where ρ_1 and ρ_2 are constants for the particular sample, B_2 depends on the thermal activation energy of the principal conduction mechanism, and

$$B_2 = \frac{U}{R}$$

where R is the gas content, U the activation energy in cal/mole. B_1 is a complex function depending both upon orientation and voltage

$$B_1 = B_0 - \beta\sqrt{E}$$

where B_0 is a constant for a given sample, β depends on the orientation and E is the field strength in volts/cm. If the temperature is made constant for a given sample, Sarzhevskii's equation reduces to Frenkel's.

A number of measurements of resistivity were made at different temperatures, varying the voltage in 150 volt steps from 150 to 1200 volts while holding the temperature constant. One set of measurements was made on a quartz plate through which current had been passed for only a few days. Another set was later made on the same plate after current had passed through it for over two months. These measurements are plotted in Figs. 14 and 15 as the common logarithm of the resistivity vs. the square root of the field strength in volts/cm.

For the short term mechanism; that is, those modes of conduction that depend on the presence of impurity ions, Fig. 13 indicates that the resis-

TABLE 5. ACTIVATION ENERGIES OF THE CONDUCTION MECHANISMS IN QUARTZ, AND ABSOLUTE VALUES OF THE RESISTIVITY

Author	Temp (° C.)	Resistivity (ohm-cm.)		Ratio $\frac{eq}{ax}$	Activation energy (kcal./mole)				Constant A
		Axial	Equat.		Axial		Equat.		
					High	Low	High	Low	
Curie	20	1×10^{14}	3×10^{16}	300					
Thornton	17	2×10^{14}	1.53×10^{16}	131					
Richardson	26.5	2×10^{13}	4.3×10^{15}	215					
Joffé	25	1×10^{13}	1×10^{19}*	1×10^{6}					
	500	1.6×10^{2}	5.6×10^{8}	3.5×10^{6}		24.4		22.5	7.26×10^{-4}
Rochow	500	—	4.75×10^{11}						
	1200	—	9.1×10^{5}				42.9		2.36
Verhoogen	500	2×10^{9}	—			23			
Sarzhevskii	560	—	3.81×10^{8}				42		
	302	—	2.51×10^{13}						
	178	—	1.0×10^{16}					21	2.63×10^{5}
Bottom	25	2.24×10^{13}				17.7			2.86
(Clear)	500	2.9×10^{5}							
Bottom	12	1.26×10^{16}				22.9			0.0405
(Smoky)	298	2.09×10^{7}							
Bottom	12	4.17×10^{16}				20.9			4.66
(Synthetic)	417	1.78×10^{7}							
King	107	9.12×10^{17}			35.5				2.33
Natural	177	6.03×10^{16}				13.4			1.95×10^{10}
	461	1.45×10^{10}							
King	111	5.76×10^{17}			39.0				
(Synthetic)	230	2.40×10^{15}				11.1			2.2×10^{11}
	460	1.00×10^{10}							
Strauss	203	1.0×10^{10}	4.0×10^{14}	4.0×10^{4}		18.4			42.6
	496	6.3×10^{6}	7.96×10^{8}	127				31.3	1.17
Wenden	529	1.28×10^{9}				24.2			362
(Disc 9)	321	2.58×10^{11}							
Wenden	528	1.64×10^{9}			39.9				0.025
(Disc 10)	365	9.57×10^{11}							
Wenden	535	1.65×10^{9}			39.5				24.55
(Disc 11)	390	3.42×10^{11}							
	279	1.54×10^{14}							
Wenden	177	3.30×10^{8}				25.0			0.0024
(Disc 12)	121	2.73×10^{10}							
	76	2.99×10^{12}							
Wenden	500	4.65×10^{6}				24.2			1.34
(Disc 13)	156	1.32×10^{12}							
Wenden	499	—	2.25×10^{7}					25.1	1.97
(Disc 15)	205	—	4.98×10^{11}						
Wenden	490	3.88×10^{8}			36.0				0.0205
(Disc 6)	302	4.78×10^{11}							
	168	1.18×10^{16}							

TABLE 5A. EXPLANATION OF DISC NUMBERS IN TABLE 5

Disc No.	Cut	Electrodes		Field strength (volts/cm)	Time of passage of current
		Cathode	Anode		
6	51°40′	Au	Pt	2450	2000h
8	Z	Pt	Pt	1880	100h
9	Z	Pt	Pt	1880	100h
10	Z	Pt	Pt	1880	282h
11	Z	Pt	Pt	1880	1400h
12	Z	Ag	Ag	1880	15m
13	Z	Pt	NaCl	156	108h
15	X	Pt	NaCl	156	60h

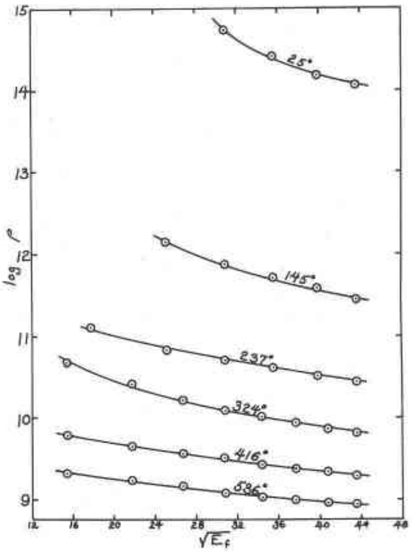

FIG. 14. Logarithm of resistivity vs. the square root of the field strength in volts/cm for a number of temperatures. Disc No. 11 after passage of current for 100 hours.

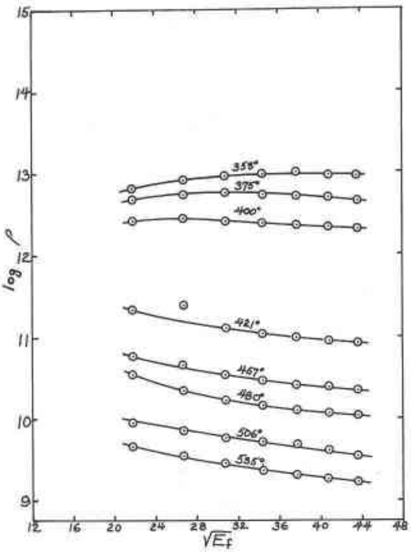

FIG. 15. Logarithm of resistivity vs. the square root of the field strength in volts/cm for a number of temperatures. Disc No. 11 after passage of current for 1400 hours.

tivity is decreased with increased field intensity at all temperatures. This observation is in agreement with the findings of Shaposhnikov, Klarmann and Mühlenpfordt (1938), Strauss (1955) and almost all investigators who have commented on the voltage dependence of the resistivity.

In the series of measurements made on the sample after passage of current for two months, it appears, below 375° C., that increase in field strength produces an increase in resistivity, whereas for higher temperatures there is an apparent decrease in resistivity for increased field strength. In no case do the plotted values indicate a strictly constant value for β in Frenkel's formula, although both Frenkel's and Sarzhevskii's equations yield close approximations to the measured resistivities at most temperatures. Agreement with Frenkel's formula is closest at the higher temperatures in both the short term and long term measurements. The factor of time clearly enters this relationship as it does all other aspects of the resistivity.

Frenkel has attributed the decrease in resistivity at higher field intensities to the excitation of an electronic mode of conduction by the freeing of electrons in the vicinity of lattice defects or interstitial impurity ions. Since the ejection of electrons in this way depends on the presence of impurity ions, it is reasonable to suppose that passage of current for long periods of time, reducing the number of such ions, may well produce the observed diminution or reversal of the effect of increased field strength.

VARIATION OF RESISTIVITY WITH CRYSTALLOGRAPHIC ORIENTATION

One of the most frequently repeated statements concerning the resistivity of quartz is that the axial resistivity is thousands of times smaller than the equatorial resistivity. This statement is, however, true only for axial resistivities that have been measured a short time after the application of potential, and which measure the mobility of impurity ions rather than the resistivity of quartz. The facts seem to indicate that when the measuring potential has been applied for a sufficiently long time the axial resistivity increases to the same order of magnitude as the equatorial resistivity. Figure 12 shows this clearly. Disc No. 12, as explained above, was deliberately measured in such a way as to obtain the values of resistivity and activation energy associated with the short-term ionic surge current. The axial resistivities found for Disc No. 12 are between three and four orders of magnitude smaller than Sarzhevskii's values for equatorial resistivity. On the other hand, Disc No. 11, after passage of current for eight weeks afforded values of axial resistivity that are almost identical with Sarzhevskii's for equatorial resistivity, and lie near the mean of Strauss' and Rochow's values for equatorial resistivity. There is as much difference between different investigators' values for equatorial resistivity as there is between the mean of the nearly identical axial resistivities of King and Wenden, and the mean of the various curves for equatorial resistivity. The difference between the axial and equatorial resistivity seems to be about of the same magnitude as the experimental error.

There is evidence that ionic diffusion may take place in directions other than parallel to *c*, and may well enter into the recorded values for equatorial resistivity. The actual relation between axial and equatorial resistivity will only be clarified when both quantities have been measured with a precision higher than that of the present study, and with equally careful precautions against inclusion of impurity-connected currents. There seems to be at least an indication that the difference between axial and equatorial resistivity is really small, comparable with the birefringence and the difference in other vectorial properties of quartz.

An interesting outgrowth of the present study has been the measurement of the resistivities of a series of quartz plates cut at different angles to the *c* axis. These slices were prepared by the Cambridge Thermionic Corp. and the orientation checked by a combination of optical and *x*-ray methods. Electrodes of Du Pont Liquid Bright Platinum #6455 were fired on and the resistivity measured at 500° C. Twelve such samples were measured, the temperature and voltage being held constant and the current noted after twenty-four hours. Table 6 records the results of this experiment. Although it is too early to express a firm opinion, there seems to be a systematic relationship between orientation and resistivity that will probably become clearer and more consistent when longer runs are made and the effect of impurity ions more clearly delineated.

TABLE 6. VARIATION OF RESISTIVITY WITH CRYSTALLOGRAPHIC ORIENTATION

Disc No.	Orientation (angle $\wedge$ *c*)	Resistivity at 500° C. (ohm-cm.)		
		4 hrs.	8 hrs.	24 hrs.
1	0°	6.65×10^6	6.65×10^6	7.98×10^6
2	10°15′	2.63×10^6	2.85×10^6	3.15×10^6
3	20°10′	2.52×10^6	2.78×10^6	3.52×10^6
4*a*	30°	2.26×10^6	2.60×10^6	4.06×10^6
4*b*	29°50′	2.52×10^6	2.85×10^6	4.35×10^6
5	42°	2.12×10^6	2.66×10^6	3.52×10^6
6	51°40′	$6.0\ \times10^6$	$6.0\ \times10^6$	$6.0\ \times10^6$
7	60°	—	1.20×10^7	1.50×10^7
8*a*	70°	3.52×10^7	4.13×10^7	5.09×10^7
8*b*	73°	7.25×10^7	7.72×10^7	8.55×10^7
9*a*	80°	2.18×10^8	2.39×10^8	2.69×10^8
9*b*	80°	2.37×10^8	2.55×10^8	2.92×10^8

For short times of passages of current the resistivity is, as Mott and Gurney say, "structure-sensitive"; that is, the current that is carried chiefly by impurity ions is greatly influenced as to magnitude and direction by the structure of the quartz. Examination of a carefully constructed model (Fig. 16) of the low-quartz structure reveals that, in addition to the often-described "tunnels" or "pores" parallel to the *c* axis, there are similar continuous openings through the structure parallel to the *a* axes, and in directions inclined about 59° to the *c* axis, nearly perpendicular to the sheets of tetrahedra underlying the major rhombohedron. These two latter sets of "pores" have an opening area in projection somewhat smaller than those parallel to *c*, and in the case of the *a* axis tunnels, have about the same center to center spacing. In the case of the inclined openings, however, the center to center spacing in projection is about 1.75 Å, as contrasted with about 2.5 Å for the *c* axis channels projected on the base. It is difficult to believe that these openings are wholly without influence on the short-term, or structure-sensitive, part of the resistivity-time relationship in equatorial and inclined sections. Experiments now in progress, as well as Disc No. 13, which was

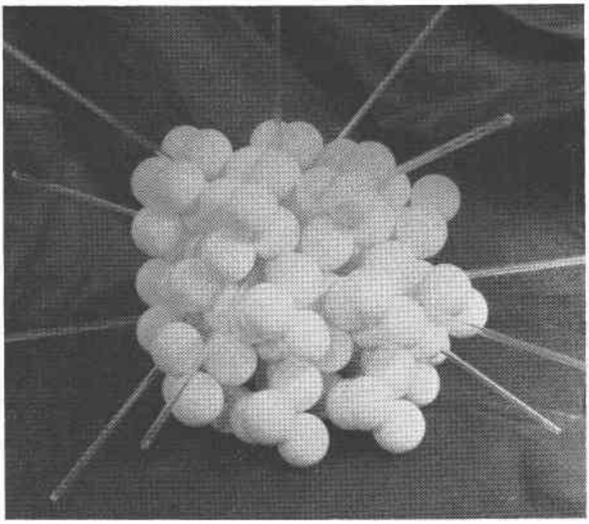

FIG. 16. Packing model of low quartz. Rods indicate the position of channels through the structure. The center vertical rod is parallel to the *c* axis. Model constructed by Ivan Barnes.

an ionic diffusion run using an X-cut plate, indicate that these channels do permit some ionic diffusion in directions other than parallel to *c*.

One very long run of over 2000 hours total duration was made using a test plate inclined 51°40′ to the *c* axis. The results of this run are given in Table 5 and Fig. 12 as Disc. No. 6. The high activation energy and uniform slope of the resistivity-temperature curve for this disc indicate that short-term ionic mechanisms do not play a significant part in the plotted values. The long duration of the run further guarantees exclusion of impurity ion connected effects. Nevertheless, the resistivity of this disc is less by one to two decades than the resistivity of Disc No. 11 which had passed current for a comparable length of time, but was Z cut. Since this is an isolated measurement unsupported by other long-term measurements on inclined plates, it is not safe to generalize from the results, but there is at least the suggestion that some directions in quartz conduct more readily than the *c* axis.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge my indebtedness to Prof. C. S. Hurlbut, for his kind help and counsel at all stages of the research, for his critical reading of the manuscript and his many constructive suggestions. I wish also to thank Mr. Richard Collette for many helpful suggestions respecting laboratory practice, and Mr. Ivan Barnes for his assistance with some of the calculations. Financial support for a part of the work was furnished by the U. S. Army Signal Corps under contract DA 36-039-sc-56689.

REFERENCES

BOTTOM, V. E. *et al.* (1953), Final Report; Signal Corps Contract DA 36-039-sc-66, Colo. A & M Coll., Ft. Collins, Colo.

FIELD, R. F. (1944), Interpretation of current-time curves, General Radio Co., Cambridge, Mass. (Privately dupl. report)

FRONDEL, C., AND HURLBUT, C. S. (1953), Final Report: Signal Corps Contract DA 36-0390sc-15350, Harvard Univ., Cambridge, Mass.

GIBSON, G., AND VOGEL, R. C. (1950), Migration of lithium and several multicharged ions through quartz plates in an electric field II, *J. Chem. Phys.*, **18,** 1094–1097.

HARRIS, P. M., AND WARING, C. E. (1937), Diffusion of lithium ions through quartz in an electric field, *Jour. Phys. Chem.*, **41,** 1077.

JOFFÉ, A. F. (1928), The physics of crystals, McGraw-Hill, New York.

JOST, W. (1952), Diffusion in solids, liquids and gases, Academic Press.

KING, J. C. (1955), Second Interim Report: Signal Corps Contract DA 36-039-sc-64586, Bell Telephone Labs., Inc., Whippany, N.J.

KING, J. C. (1956), Fifth Interim Report: Signal Corps Contract DA 36-039-sc-64586, Bell Telephone Labs., Inc., Whippany, N. J.

MOTT, N. F. AND GURNEY, R. W. (1948), Electronic processes in ionic crystals, Oxford.

ROCHOW, E. G. (1938), Electrical conductivity in quartz. *Jour. App. Phys.*, **9,** 664–669.

SARZHEVSKII, P. E. (1952), *Doklady Akad. Nauk SSRR*, **82,** 571–574 (In Russian) Reviewed by J. M. Hough in *Sci. Abst.*, **55,** (1952).

SOSMAN, R. B. (1927), The properties of silica, Chemical Catalog Co., New York. All references prior to 1927 are reviewed in this work.

STRAUSS, S. W. *et al.* (1956), Fundamental factors controlling electrical resistivity in vitreous ternary lead silicates, *J. Res. Nat. Bur. Stand.*, **56,** 135–142.

STUART, M. R. (1955), Dielectric constant of quartz as a function of frequency and temperature, *J. App. Phys.*, **26,** 1399–1404.

VERHOOGEN, J. (1952), Ionic diffusion and electrical conductivity in quartz, *Am. Mineral.*, **37,** 637–655.

VOGEL, R. C., AND GIBSON, G. (1950), Migration of sodium ions through quartz plates in an electric field, *J. Chem. Phys.*, **18,** 490–494.

WENDEN, H. E. (1954), Second Quarterly Report: Signal Corps Contract DA 36-039-sc-56689, Harvard Univ., Cambridge, Mass.

WENDEN, H. E. (1954a), Third Quarterly Report: Signal Corps Contract DA 36-039-sc-56689, Harvard Univ., Cambridge, Mass.

WENDEN, H. E. (1955), Interim Report; Signal Corps Contract DA-36-039-sc-56689, Harvard Univ., Cambridge, Mass.

WENDEN, H. E. (1956), Final Report: Signal Corps Contract DA 36-039-sc-56689, Harvard Univ., Cambridge, Mass.