Ionic conductivity of quartz: DC time dependence and transition in charge carriers

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Abstract

The time dependence of DC electrical conductivity in the c-axis direction of quartz can be accounted for by a transition in charge carriers from interstitial alkali impurities to interstitial H. The diffusive transport rates of Li, Na, and K are rapid parallel to c and have been shown to be responsible for the highly anisotropic electrical conductivity measured at short times. With increasing time, however, conductivities parallel to c decrease progressively to values that are roughly equal to those measured perpendicular to c. Comparison of these ultimate, nearly isotropic conductivities with those derived from recent measurements of H diffusion parallel and perpendicular to c suggests that H interstitials are the principal charge carriers at long times. The transient decrease in conductivities parallel to c is interpreted to result from depletion of initial alkali impurities, whereas the steady-state conductivities measured at long times may be sustained by the steady supply of H by the dissociation of atmospheric water vapor. The mobility of H along the c axis is anomalously low and at variance with the trend of increasing mobility with decreasing ionic radius exhibited by Cs, Rb, K, Na, and Li. Although the elastic lattice distortions required for H transport are insignificant in comparison with those required by the larger alkali impurities, the strong association of H interstitials with Al substitutions for Si may be responsible for the relatively low H mobilities.

Introduction

Just 100 years ago, Jacques Curie (1886, 1889) and E. Warburg and F. Tegetmeier (1887, 1888) made the first measurements of the direct current ionic conductivity in quartz. In these earliest studies of the electrical properties of minerals, Curie and Warburg and Tegetmeier made key observations that have endured a century of research on quartz conductivities, and they proposed mechanisms of charge transport that resemble current models. Curie discovered that the DC conductivity of quartz in the c-axis direction depends upon time (the current decaying exponentially with time) and proposed an electrolytic model of charge transport involving molecular water and dissolved salts in the c-axis channels. Likewise, Warburg and Tegetmeier recognized the time dependence of conductivity in quartz and suggested a charge-transport mechanism involving the migration of Na ions initially present as impurities in the quartz structure. Since these pioneering studies, measurements of conductivity in quartz have been extended to temperatures of up to 1200°C and DC excitation times ranging from 0.5 to 10⁶ s (as well as AC frequencies from 20 to 10⁷ Hz), both for...
natural and synthetic crystals in the c-axis direction and perpendicular to it. Alkali impurities, as originally proposed, are now known to be important charge carriers accounting for DC conductivities (and AC conductivities) measured at short times parallel to c.

On the centennial of the original experiments of electrical properties of quartz, we commemorate these early experimental mineralogists and take this opportunity to compare the DC conductivities of quartz measured at long times with recent results obtained for H diffusion. On this basis we proposed a model for steady-state charge transport involving interstitial H. Although the long-time conductivity of quartz is unlikely to control the bulk electrical properties of rocks in which intergranular fluids carry much of the current, determination of its mechanisms should help to evaluate the defect chemistry of quartz and its effects on such diverse phenomena as coloration (Cohen, 1960; Kreft, 1975; Weil, 1975; Halliburton et al., 1981), hydrolytic weakening (Griggs and Blacic, 1965; Hirsch, 1981; Hobbs, 1981), and Si and oxygen diffusion (Dennis, 1984; Giletti and Yund, 1984) by placing constraints on defect mobilities and internal charge transport.

**ELECTRICAL CONDUCTIVITY OF QUARTZ**

The electrical conductivity of quartz measured at short DC times, or under alternating currents, is extremely anisotropic with conductivities parallel to c exceeding those measured perpendicular to c by more than 10^6 (Joffe, 1928; Rochow, 1938; Sarzhevskii, 1952; Strauss et al., 1956; Wenden, 1957; Glushkova and Firsova, 1968). Corresponding to this anisotropy, the diffusive transport rates of alkali impurities occupying interstitial sites along the c-axis channels have been shown to be rapid (Harris and Waring, 1937; Vogel and Gibson, 1950; Gibson and Vogel, 1950; Verhoogen, 1952; Stuart, 1955; Wenden, 1957; Milne and Gibbs, 1964; Snow and Gibbs, 1964; Rybach and Laves, 1967; Frischat, 1969, 1970a, 1970b), suggesting that they are the principal charge carriers in the c-axis direction. With increasing time, however, DC conductivities measured parallel to c decrease by several orders of magnitude approaching those measured perpendicular to c. Corresponding AC conductivities measured parallel to c do not show time-dependent behavior but are affected by prior application of DC fields.

In a study explicitly designed to investigate the time dependence of c-axis conductivities, Wenden (1957) measured DC conductivities (Fig. 1) for times of up to 5 x 10^6 s (1400 h) and showed that much of the scatter in reported DC conductivities parallel to c (Fig. 2A) could be explained by variations in time of current passage. DC conductivities measured parallel to c exhibit an initial transient decrease leveling off with time to nearly steady-state values. Accompanying this transition, the apparent activation energies of transient and steady-state c-axis conductivities differ, increasing from 100 to 165 kJ/mol (Wenden, 1957), respectively. Conductivities measured perpendicular to c show a far smaller transient response, and the scatter in reported DC conductivities perpendicular to c is correspondingly much smaller (Fig. 2B). Conductivities measured perpendicular to c are essentially the same as the steady-state c-axis conductivities with an apparent activation energy of 180 kJ/mol (Rochow, 1938; Sarzhevskii, 1952).

Interstitial alkali impurities have repeatedly been shown to be the principal charge carriers controlling short-time c-axis conductivities (Table 1); the transient decay of c-axis conductivities have therefore been interpreted to result from the depletion of alkalis. The mechanisms of charge transport at long DC times and those acting perpendicular to c have received less attention, and charge carriers proposed include electronic as well as ionic point defects. In this paper, we propose that intrinsic electronic conductivities have never been measured and that the isotropic long-time DC conductivities are controlled by the diffusion of interstitial H.

**DIFFUSION OF H**

The diffusion of H in quartz (Fig. 3) has been studied by measuring the rates of H uptake, H-D exchange (Kats, 1962; Kronenberg et al., 1986), and tritium uptake (Shaffer et al., 1974). At high temperature (T > 620°C), H diffusion is essentially isotropic with relatively large activation energies of 175 kJ/mol (Kats, 1962) to 200–210 kJ/mol (Kronenberg et al., 1986). Diffusion of H at temperatures below 620°C exhibits a smaller activation energy of 80 kJ/mol (Kats, 1962), associated with a change in H speciation (Kats, 1962; Aines and Rossman, 1984). Interstitial H defects at high temperatures are strongly associated with Al substitutions for Si and lead to a H solubility limit given by the local charge neutrality condition $[\text{H}^+] = [\text{Al}^3+]$ (Kats, 1962; Kronenberg et al., 1986) and the Al concentration (which may range from 60 to 300 atoms Al per 10^6 atoms Si). At low temperatures, however, H interstitials are not associated with Al centers.
Fig. 2. Collected conductivity data as a function of temperature. (A) Arrhenius plot of conductivities measured parallel to c show scatter over several orders of magnitude (Exner, 1901; Joffe, 1928; Verhoogen, 1952; Bottom, 1953; King, 1955, 1956; Strauss et al., 1956; Wenden, 1957). Wenden (1957) showed that the wide spread in reported conductivities could be explained by the decrease in conductivity with time. (B) Arrhenius plot of conductivities measured perpendicular to c (Joffe, 1928; Sarzhevskii, 1952; Rochow, 1938; Strauss et al., 1956).

to any great extent (Kats, 1962). This transition in defect chemistry, though suggestively near the transition between high (β) and low (α) quartz, does not appear to correspond exactly to the α-β transition temperature (573°C) at the near-ambient pressures (0.1 to 2.5 MPa) employed by Kats (1962).

Shaffer et al. (1974) measured H diffusion within the high temperature range (at T = 720–850°C), but their experiments were done at rather low pressures (P$_{H_2O}$ = 0.06 MPa), and their reported diffusivities are orders of magnitude smaller than those of Kats (1962, measured at $P_{H_2O} = 2.5$ MPa) and Kronenberg et al. (1986, measured at $P_{H_2O} = 890$ MPa) with activation energies (90–110 kJ/mol) comparable to that reported by Kats (1962) for lower temperatures. We speculate that this discrepancy is due to a change in H speciation at low water pressures.

**Inferred Conductivities**

Kats (1962) first proposed that H may be an important charge carrier parallel to c on the basis of comparisons of his diffusion results with DC conductivities measured at long times (Table 1). Along similar lines, White (1971) proposed that hydroxyl diffusion may be an important conduction mechanism parallel to c; however, measurements of oxygen diffusion under hydrothermal conditions (Dennis, 1984; Giletti and Yund, 1984) suggest that hydroxyl mobilities are much smaller than those of interstitial H. More recent studies of electrolytic sweeping (Lo-

<table>
<thead>
<tr>
<th>Table 1. Proposed charge carriers in quartz</th>
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<tr>
<td><strong>Point defect</strong></td>
</tr>
<tr>
<td>Li$^+$</td>
</tr>
<tr>
<td>Na$^+$</td>
</tr>
<tr>
<td>K$^+$</td>
</tr>
<tr>
<td>Rb$^+$</td>
</tr>
<tr>
<td>Cs$^+$</td>
</tr>
<tr>
<td>H$^+$</td>
</tr>
<tr>
<td>OH$^-$</td>
</tr>
<tr>
<td>e$^-$ or h</td>
</tr>
<tr>
<td>(at times &gt; 5 x 10$^4$ s)</td>
</tr>
<tr>
<td>$\perp c$</td>
</tr>
<tr>
<td>ionic ($T &gt; 300°C$)</td>
</tr>
<tr>
<td>e$'$ ($T &lt; 300°C$)</td>
</tr>
<tr>
<td>ionic (short times)</td>
</tr>
<tr>
<td>e$'$ or h (long times)</td>
</tr>
</tbody>
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Table 2. Activation energies for c-axis diffusion

<table>
<thead>
<tr>
<th>Point defect</th>
<th>$E^*$ (kJ/mol)</th>
<th>References</th>
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<tbody>
<tr>
<td>H⁺</td>
<td>175 ($T &gt; 620^\circ$C)</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>200–210</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>80 ($T &lt; 620^\circ$C)</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>90–110</td>
<td>8</td>
</tr>
<tr>
<td>Li⁺</td>
<td>72–90</td>
<td>1</td>
</tr>
<tr>
<td>Na⁺</td>
<td>90–105</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>102</td>
<td>5</td>
</tr>
<tr>
<td>K⁺</td>
<td>84</td>
<td>6</td>
</tr>
<tr>
<td>Rb⁺</td>
<td>88</td>
<td>7</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>133</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>117</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>125</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>138</td>
<td>7</td>
</tr>
</tbody>
</table>


Fig. 3. Arrhenius plot of collected diffusion data for H in quartz. H diffusion is nearly isotropic with relatively large activation energies ($E^* = 175$ kJ/mol, Kats, 1962; $E^* = 200–210$ kJ/mol, Kronenberg et al., 1986) at high temperatures ($T > 620^\circ$C) and a smaller activation energy ($E^* = 80$ kJ/mol, Kats, 1962) at low temperatures ($T < 620^\circ$C). The diffusivities reported by Shaffer et al. (1974) are orders of magnitude smaller than those of Kats (1962) and Kronenberg et al. (1986).

Fig. 4. Inferred conductivities due to Na and H migration form an envelope around conductivities measured parallel to c. For directions perpendicular to c, the mobilities of H and Na are rather similar, and either defect may account for the observed conductivities. The time dependence of conductivities parallel to c can therefore be explained by a transition in charge carriers from initial alkali interstitials to interstitial H (Fig. 5). The inferred conductivities due to the diffusion of Li, Na, K, and Cs (Verhoogen, 1952; Rybach and Laves, 1967; Frischat, 1969, 1970a, 1970b; White, 1970) compare favorably with the initial conductivities measured by Wenden (1957); the inferred conductivities due to H diffusion (Kats, 1962; Kronenberg et al., 1986) compare more favorably with the ultimate, steady-state conductivities. H, unlike the initial alkali impurities, can be supplied at a steady rate by dissociation of atmospheric water vapor at the anode, giving rise to steady-state conductivities. Transient conductivities at intermediate times may thus be modeled, though we have not explicitly done so, by solving for charged defect mobilities corresponding to simultaneous gradients in their concentrations and in the electrical potential.

Comparison of Interstitial H and Alkali Mobilities

Although the transition from alkali to H charge carriers appears to explain the behavior of quartz c-axis conductivities, the low rates of H diffusion relative to those of the alkalis requires discussion. Because alkali and H interstitials have the same effective charge, their relative mobilities might be expected to correlate inversely with the lattice distortions required for their migration. Accordingly, the rates of diffusion for the alkalis along the c
Fig. 4. Comparison of inferred conductivities based on H (Kats, 1962; Shaffer et al., 1974; Kronenberg et al., 1986) and Na (Frischat, 1970b) diffusivities with the collected conductivity data (shown in Fig. 2) parallel (A) and perpendicular (B) to c.

axis of quartz exhibit a systematic variation of increasing mobility with decreasing ionic radius (Fig. 6). When compared with this trend, however, the diffusion of interstitial H is anomalously slow.

On the basis of the high-temperature association of H with Al impurities, we suggest that the anomalously low mobilities of H result from a large association enthalpy that must be overcome for diffusion. Both alkali and H interstitials have been shown to act as charge-compensating defects for Al substitutions for Si (Bambauer, 1961; Bambauer et al., 1962, 1963; Kats, 1962; Stevels and Volger, 1962; Snow and Gibbs, 1964; King and Sander, 1972; Park and Nowick, 1974; Markes and Halliburton, 1979; Weil, 1975; Halliburton et al., 1981; Jain and Nowick, 1982a, 1982b). However, the alkalis, residing in the c-axis channels (Fig. 7) form an essentially ionic bond with the Al center, whereas H is expected to bond to a bridging oxygen and requires much larger energies to remove (Sykes and Weil, 1970; Nuttall and Weil, 1981). Corresponding to this additional bonding, the activation energies for H diffusion in the c-axis direction of quartz (at temperatures greater than 620°C) appear to be larger than those determined for alkali diffusion (Table 2). Thus, once removed from an Al site, H is expected to have a greater mobility than those of the larger alkali interstitials; the large Al-H pair enthalpy must first be overcome, however, to form an unassociated (or free) H interstitial. Unlike the larger alkalis, free H interstitials are not restricted to the c-axis channels and may migrate perpendicular to c at the same rates as those parallel to c. At low temperatures (T < 620°C), H interstitials occur at numerous sites unrelated to Al impurities (Kats, 1962), and here the activation energies are more comparable with those for alkali diffusion.

**Model of H Diffusion**

We propose a model for H diffusion, which in some respects resembles that of Jain and Nowick (1982a) for interstitial alkalis, wherein we distinguish between H interstitials that are associated with Al\(_c\) and H that is not.
Fig. 5. Inferred c-axis conductivities based on alkali (Li, Verhoogen, 1952, and White, 1970; Na, Verhoogen, 1952, Rybach and Laves, 1967, and Frischat, 1970b; K, Verhoogen, 1952; Cs, White, 1970) and H (Kats, 1962; Shaffer et al., 1974; Kronenberg et al., 1986) diffusion at (and, in some cases, extrapolated to) $T = 500{}^\circ$C. The inferred hydroxyl conductivity of White (1971) is also shown. The inferred alkali conductivities compare favorably with measured conductivities at short times (fine lines, as shown in Fig. 1, taken from Wenden, 1957, for $T = 496$ and 536°C), whereas the inferred H conductivities match more closely the long-time conductivities.

Fig. 6. H and alkali diffusivities as a function of increasing ionic radius at (and extrapolated to) $T = 500{}^\circ$C (Verhoogen, 1952; Kats, 1962; Rybach and Laves, 1967; Frischat, 1970b; White, 1970, 1971; Shaffer et al., 1974; Kronenberg et al., 1986).
Kats (1962) effectively demonstrated that H interstitials at high temperatures \((T > 620^\circ C)\) are associated with Al defects but that a large number of other interstitial H sites, which are unrelated to Al centers, exist at low temperatures \((T < 620^\circ C)\). Given that Al is essentially immobile, the diffusion of H at high temperatures requires the dissociation of Al-H pairs to form free H; followed by transport to neighboring Al\(_{si}\) sites. At low temperatures, a large fraction of H interstitials is not associated with Al substitutionals (Kats, 1962; Aines and Rossman, 1984), and their mobilities do not depend on H-Al dissociation. With this interpretation, the change in activation energy of H diffusion at low and at high temperatures may represent the enthalpy required to remove H interstitials from Al sites.

If, at high temperatures, H diffusion occurs by the motion of H; from one Al\(_{si}\) site to another, its diffusion coefficient \(D\) can be expressed (Shewmon, 1963) as

\[
D = k\alpha^2 C_d w, \tag{2}
\]

where \(\alpha\) is the mean Al-Al spacing (\(-7 \text{ nm for an Al concentration of 100 ppm}\)), \(C_d\) is the concentration of uncompensated Al sites, \(w\) is the probability that a free H; will jump to a neighboring Al\(_{si}\) site, and \(k\) is a geometric factor. At equilibrium, the concentrations of both mobile H; and uncompensated Al\(_{si}\) are given by

\[
C_d = \left[\exp(\Delta S_d/R)\right] \left[\exp(-\Delta H_d/RT)\right], \tag{3}
\]

where \(\Delta S_d\) and \(\Delta H_d\) represent the changes in entropy and enthalpy, respectively, of the crystal for each H; removed from an Al\(_{si}\) site. Similarly, the probability that a free H; will jump to a particular Al\(_{si}\) site is given by

\[
w = \nu\left[\exp(\Delta S_m/R)\right] \left[\exp(-\Delta H_m/RT)\right], \tag{4}
\]

where \(\Delta S_m\) and \(\Delta H_m\) are the entropy and enthalpy, respectively, of the H mobility and \(\nu\) is the frequency with which H; defects midway between two Al sites will move to the new site. Combining Equations 2, 3, and 4,

\[
D = k\nu\alpha^2 \left[\exp((\Delta S_d + \Delta S_m)/R)\right] \left[\exp(-(\Delta H_d + \Delta H_m)/RT)\right]. \tag{5}
\]
If, at low temperatures, H is present as interstitials that are not associated with Al, its diffusion coefficient (Shewmon, 1963) is independent of concentration:

\[ D = \gamma a^2 w, \]

where \( a \) is the jump distance, \( w \) is the probability that a particular interstitial will jump, and \( \gamma \) is a geometric factor. Here, again, the probability may be expressed according to Equation 4, where \( \nu \) represents the jump frequency and \( \Delta S_m \) and \( \Delta H_m \), respectively, represent the entropy and enthalpy of H; movement, so that Equation 6 can be written

\[ D = \gamma a^2 [\exp(\Delta S_m/R)] [\exp(\Delta H_m/RT)]. \]

If we choose to define all of the parameters in Equation 7 for the same distance as the average Al-Al spacing of the crystal, we can compare the high- and low-temperature relations and interpret the measured change in activation energies (from 175 to 80 kJ/mol = 100 kJ/mol, Kats, 1962) to represent the Al-H pair enthalpy. The activation energy for H diffusion (of 80 kJ/mol, Kats, 1962) measured at low temperatures is thus interpreted to represent the enthalpy of H motion over the mean Al-Al spacing.

**CONCLUSIONS**

Comparisons of DC conductivities of quartz with diffusional transport rates of alkali interstitials and interstitial H lead to the following conclusions:

1. Anisotropic conductivities measured at short DC times (or under AC fields) parallel to c compare favorably with those inferred from the diffusion of interstitial alkali impurities.
2. Isotropic conductivities measured at long DC times compare favorably with those inferred from the diffusion of interstitial H.
3. The time dependence of DC conductivities parallel to c is due to the depletion of initial alkali impurities and a transition in charge carriers to interstitial H. At short times, conductivities measured parallel to c are controlled by alkali mobilities, whereas conductivities measured perpendicular to c may be controlled by either alkali or H mobilities. At long times, the nearly isotropic conductivities are controlled by the mobility of H interstitials in all directions. Apparently, intrinsic, electronic conductivities have not, as yet, been measured.
4. H diffusion parallel to c is slow relative to that of larger alkali interstitials owing to the strong association of H; with Al\(_2\).  
5. The change in activation energy for H diffusion at high and at low temperatures may represent the enthalpy required to dissociate H interstitials from Al substitutions for Si.

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**REFERENCES**


Curie, J. (1886) In Wenden, 1957, below.

--- (1889) Recherches sur la conductibilité des corps cristallisés. Annales de Chimie et de Physique, ser. 6, 18, 202-209.


Exner (1901) In Wenden, 1957, below.


Gibson, G., and Vogel, R.C. (1950) Migration of lithium and several multicharged ions through quartz plates in an electric field II. Journal of Chemical Physics, 18, 1094-1097.


Kreiff, G.B. (1975) Effects of high-temperature electrolysis on the color-
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