

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

A. K. KRONENBERG

Geophysics Department, Texas A&M University, College Station, Texas 77843, U.S.A.

S. H. KIRBY

U.S. Geological Survey, 345 Middlefield Road, M.S. 977, Menlo Park, California 94025, U.S.A.



Commemorative photograph of Jacques and Pierre Curie (left and right, respectively) in 1878. Courtesy of S. Leher, Centre de Ressources Historiques, ESPCI, Paris.

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 ex-

ponentially 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

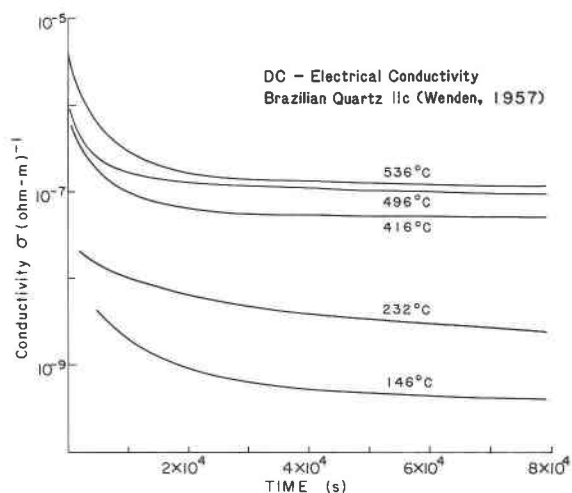


Fig. 1. Direct current conductivities measured parallel to *c* as a function of time (after Wenden, 1957).

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; Krefft, 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 10^3 (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 5×10^6 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 ($T > 620^\circ\text{C}$), 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 $[\text{H}_i] = [\text{Al}_i]$ (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

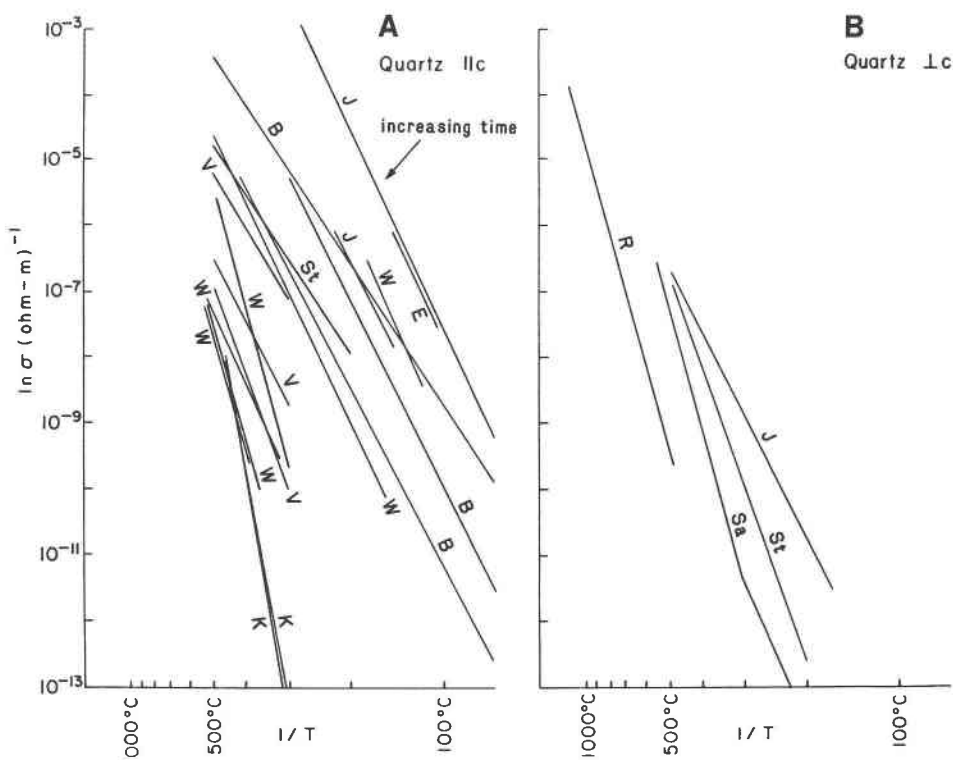


Fig. 2. Collected conductivity data as a function of temperature. (A) Arrhenius plot of conductivities measured parallel to *c* show scatter over several orders of magnitude (Exner, 1901; Joffe, 1928; Verhoogen, 1952; Bottom, 1953; King, 1955, 1956; Strauss et al., 1956; Wenden, 1957). Wenden (1957) 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 ($P_{\text{H}_2\text{O}} \approx 0.06$ MPa), and their reported diffusivities are orders of magnitude smaller than those of Kats (1962, measured at $P_{\text{H}_2\text{O}} = 2.5$ MPa) and Kronenberg et al. (1986, measured at $P_{\text{H}_2\text{O}} = 890$ 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, measure-

ments 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 1. Proposed charge carriers in quartz

	Point defect	References*
<i>c</i>	Li ⁺	2, 4, 7, 8, 11, 13, 14
	Na ⁺	1, 2, 5, 7, 9, 11, 13, 14
	K ⁺	7, 11
	Rb ⁺	11
	Cs ⁺	11
	H ⁺	10, 14
	OH ⁻	12
	e ⁻ or h ⁺	9
	(at times > 5×10^5 s)	
⊥ <i>c</i>	e ⁻	3
	ionic ($T > 300^\circ\text{C}$)	6
	e ⁻ ($T < 300^\circ\text{C}$)	
	ionic (short times)	9
	e ⁻ or h ⁺ (long times)	

* 1, Warburg and Tegetmeier, 1888; 2, Harris and Waring, 1937; 3, Rochow, 1938; 4, Gibson and Vogel, 1950; 5, Vogel and Gibson, 1950; 6, Sarzhevskii, 1952; 7, Verhoogen, 1952; 8, Stuart, 1955; 9, Wenden, 1957; 10, Kats, 1962; 11, White, 1970; 12, White, 1971; 13, Jain and Nowick, 1982a, 1982b; 14, Lopez et al., 1986.

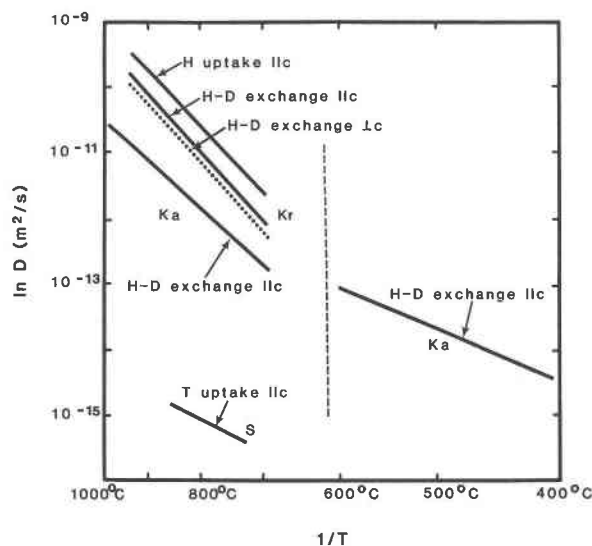


Fig. 3. Arrhenius plot of collected diffusion data for H in quartz. H diffusion is nearly isotropic with relatively large activation energies ($E^* = 175$ kJ/mol, Kats, 1962; $E^* = 200$ – 210 kJ/mol, Kronenberg et al., 1986) at high temperatures ($T > 620^\circ\text{C}$) and a smaller activation energy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

pez et al., 1986) and measurements of H diffusion both parallel and perpendicular to *c* (Kronenberg et al., 1986) have confirmed the original results of Kats (1962) and have shown that the diffusion of H in quartz is nearly isotropic. Ionic conduction in quartz due to H diffusion may therefore be expected to be isotropic.

Given the identification of H defects as charged interstitials with concentrations (given by the local charge neutrality condition $[\text{H}_i^-] = [\text{Al}_{\text{Si}}]$) of the order of 100 ppm (atoms H per 10^6 atoms Si), the expected conductivities due to H diffusion can be determined using the relationship between ionic conductivity and tracer diffusion, as derived from the Nernst-Einstein relationship:

$$\sigma = c_i q_i^2 D / kT, \quad (1)$$

where c_i is the concentration of charged interstitial defects, q_i is the charge of these interstitial defects, D is the tracer diffusion coefficient, k is Boltzmann's constant, and T is the temperature in kelvins (Shewmon, 1963). Likewise, we can estimate the conductivities due to the diffusion of alkali interstitials assuming their initial concentrations are also limited by the initial Al content (again we use 100 ppm). Although the alkalis may be present at these concentrations initially, they are expected to be depleted with time under a DC field.

Making use of the above relation and tracer-diffusion results for Na_i^- (Frischat, 1969, 1970a, 1970b) and H_i^- (Kats, 1962; Shaffer et al., 1974; Kronenberg et al., 1986) we compare inferred conductivities (Fig. 4) with the collected measured conductivities. The inferred conductiv-

TABLE 2. Activation energies for *c*-axis diffusion

Point defect	E^* (kJ/mol)	References*
H_i^-	175 ($T > 620^\circ\text{C}$)	4
	200–210	9
	80 ($T < 620^\circ\text{C}$)	4
	90–110	8
Li_i^-	72–90	1
	86	3
	75	7
Na_i^-	90–105	2
	100	3
	102	5
	84	6
	88	7
K_i^-	133	3
	117	7
Rb_i^-	125	7
Cs_i^-	138	7

* 1, Gibson and Vogel, 1950; 2, Vogel and Gibson, 1950; 3, Verhoogen, 1952; 4, Kats, 1962; 5, Rybach and Laves, 1967; 6, Frischat, 1969, 1970a, 1970b; 7, White, 1970; 8, Shaffer et al., 1974; 9, Kronenberg et al., 1986.

ities 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*

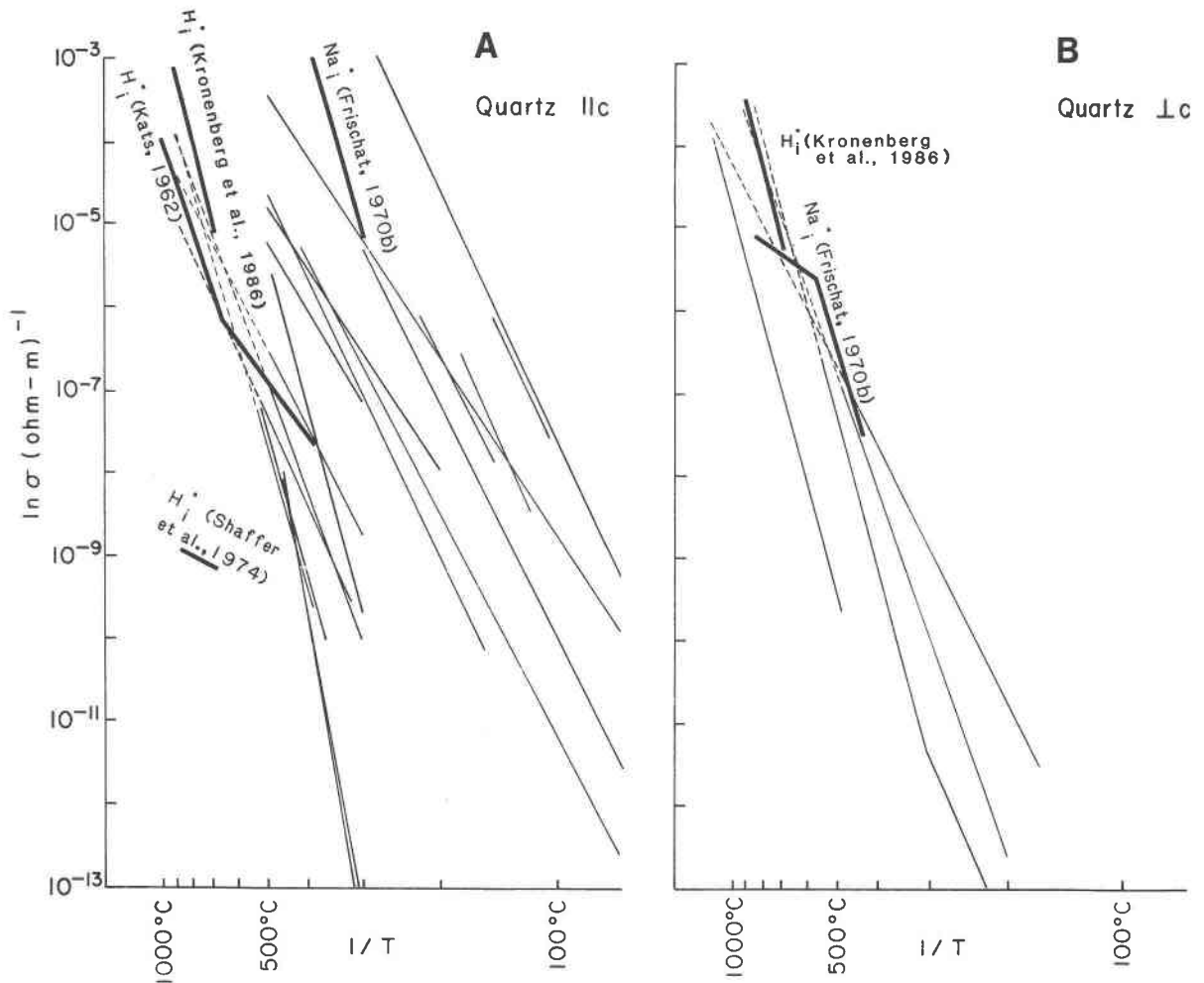


Fig. 4. Comparison of inferred conductivities based on H (Kats, 1962; Shaffer et al., 1974; Kronenberg et al., 1986) and Na (Frischat, 1970b) diffusivities with the collected conductivity data (shown in Fig. 2) parallel (A) and perpendicular (B) to *c*.

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 ($T < 620^\circ\text{C}$), 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'_{Si} and H that is not.

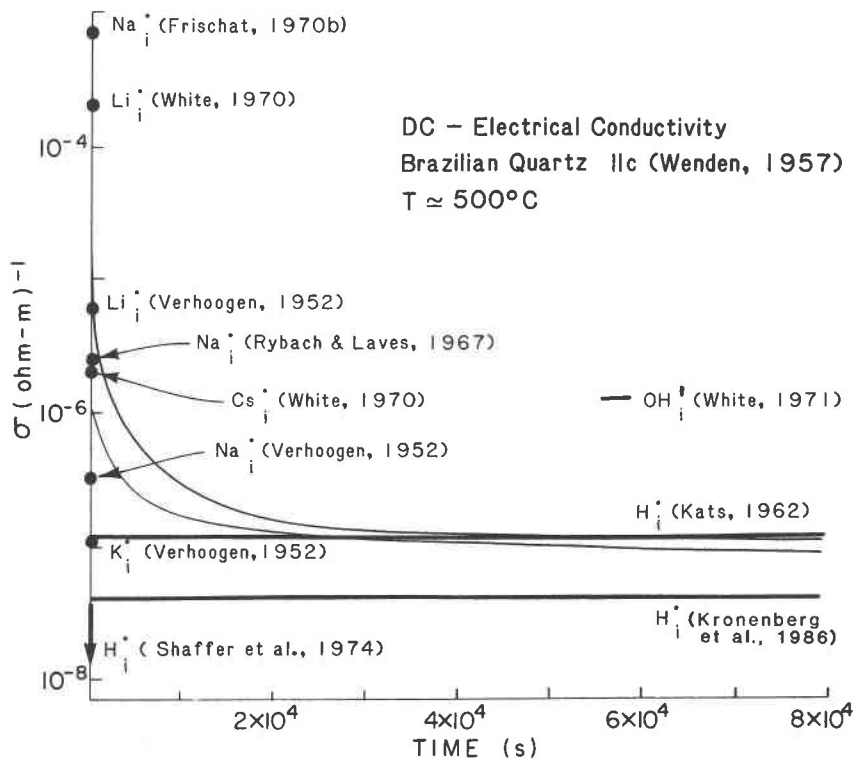


Fig. 5. Inferred c-axis conductivities based on alkali (Li, Verhoogen, 1952, and White, 1970; Na, Verhoogen, 1952, Rybach and Laves, 1967, and Frischat, 1970b; K, Verhoogen, 1952; CS, White, 1970) and H (Kats, 1962; Shaffer et al., 1974; Kronenberg et al., 1986) diffusion at (and, in some cases, extrapolated to) $T = 500^{\circ}\text{C}$. 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.

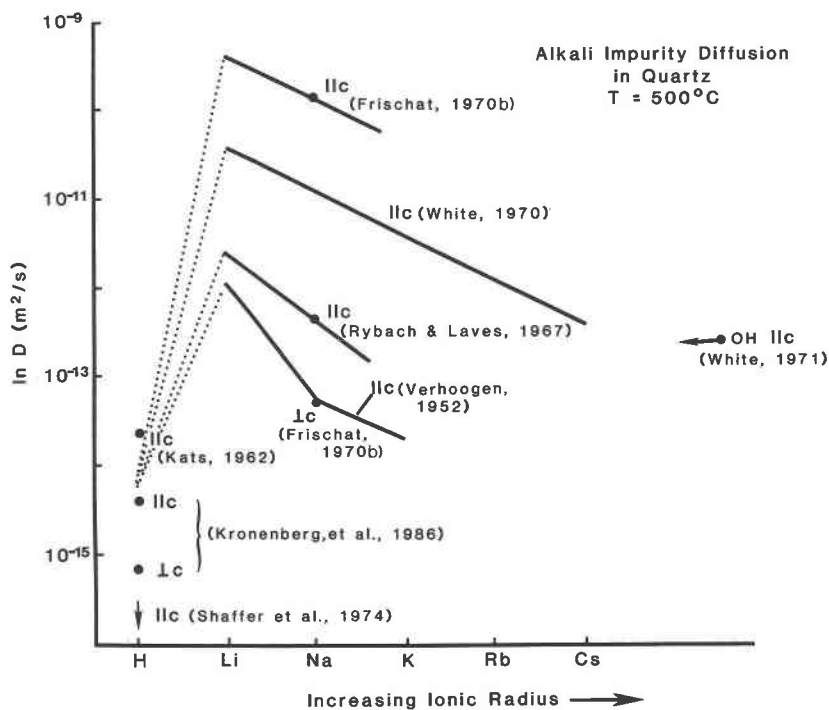


Fig. 6. H and alkali diffusivities as a function of increasing ionic radius at (and extrapolated to) $T = 500^{\circ}\text{C}$ (Verhoogen, 1952; Kats, 1962; Rybach and Laves, 1967; Frischat, 1970b; White, 1970, 1971; Shaffer et al., 1974; Kronenberg et al., 1986).

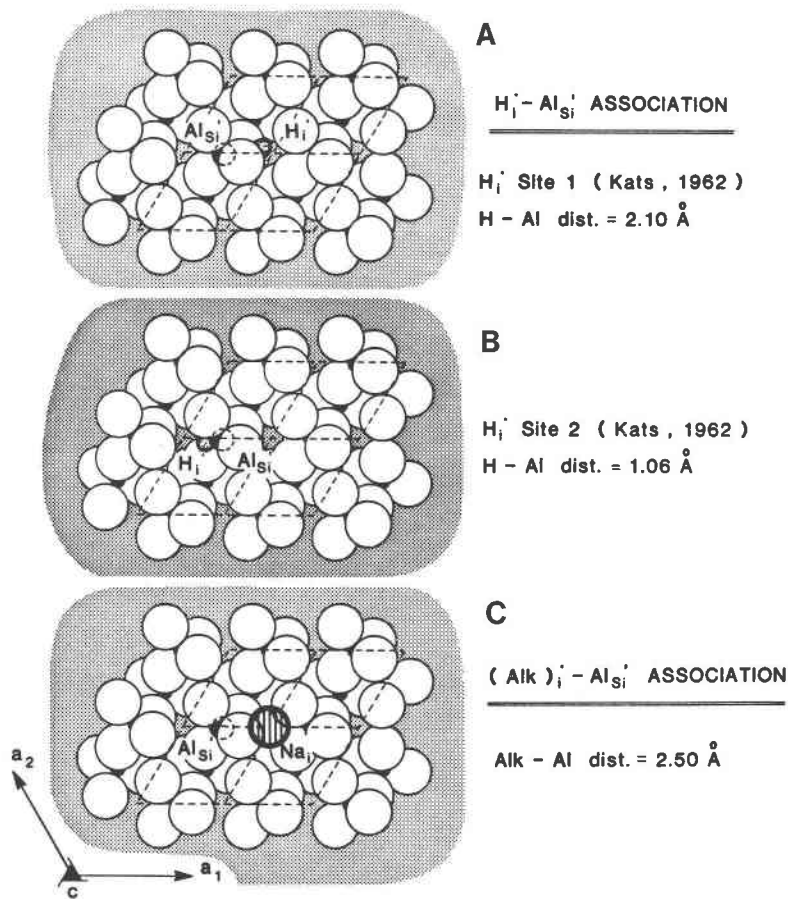


Fig. 7. Interstitial H and alkali sites associated with Al substitutionals. Al-associated H sites 1 and 2 (A and B, respectively) proposed by Kats (1962) for quartz at high temperatures (H-Al distances of 2.10 and 1.06 Å, respectively). (C) Al-associated interstitial alkalis occupy the center of the c-axis channels (H-Al distance of 2.50 Å).

Kats (1962) effectively demonstrated that H interstitials at high temperatures ($T > 620^\circ\text{C}$) 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 ($T < 620^\circ\text{C}$). Given that Al is essentially immobile, the diffusion of H at high temperatures requires the dissociation of Al-H pairs to form free H_i^- 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_i^- from one Al_{Si}^+ site to another, its diffusion coefficient D can be expressed (Shewmon, 1963) as

$$D = k\alpha^2 C_d w, \quad (2)$$

where α is the mean Al-Al spacing (~ 7 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_i^- will jump to a neighboring Al_{Si}^+ site, and k is a geometric factor. At equilibrium, the concentrations of both mobile H_i^- and uncompensated Al_{Si}^+ are given by

$$C_d = [\exp \Delta S_d / R] [\exp(-\Delta H_d / RT)], \quad (3)$$

where ΔS_d and ΔH_d represent the changes in entropy and enthalpy, respectively, of the crystal for each H_i^- removed from an Al_{Si}^+ site. Similarly, the probability that a free H_i^- will jump to a particular Al_{Si}^+ site is given by

$$w = \nu [\exp(\Delta S_m / R)] [\exp(-\Delta H_m / RT)], \quad (4)$$

where ΔS_m and ΔH_m are the entropy and enthalpy, respectively, of the H mobility and ν is the frequency with which H_i^- defects midway between two Al sites will move to the new site. Combining Equations 2, 3, and 4,

$$D = k\nu\alpha^2 [\exp((\Delta S_d + \Delta S_m) / R)] [\exp(-(\Delta H_d + \Delta H_m) / RT)]. \quad (5)$$

The empirically derived temperature dependence is thus interpreted to represent the sum of enthalpies for H dissociation from one Al site and for migration to a new Al site.

If, at low temperatures, H is present as interstitials that are not associated with Al, its diffusion coefficient (Shewmon, 1963) is independent of concentration:

$$D = \gamma\alpha^2w, \quad (6)$$

where α is the jump distance, w is the probability that a particular interstitial will jump, and γ is a geometric factor. Here, again, the probability may be expressed according to Equation 4, where ν represents the jump frequency and ΔS_m and ΔH_m , respectively, represent the entropy and enthalpy of H_i movement, so that Equation 6 can be written

$$D = \gamma\nu\alpha^2[\exp(\Delta S_m/R)][\exp(-\Delta H_m/RT)]. \quad (7)$$

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 \approx 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_i with Al_{Si} .

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.

ACKNOWLEDGMENTS

We would like to thank D. Lockner for helpful discussions and for his thoughtful review of our manuscript. We also extend thanks to R. A. Yund for discussions that helped clarify our thoughts. Many thanks go to

S. Leher and the Centre de Ressources Historiques, ESPCI, Paris for kindly providing the photograph of Jacques and Pierre Curie.

REFERENCES

- Aines, R.D., and Rossman, G.R. (1984) Water in minerals? A peak in the infrared. *Journal of Geophysical Research*, 89, 4059–4071.
- Bambauer, von H.U. (1961) Spurenelementgehalte und γ -Farbzentren in Quarzen aus Zerrklüftenden der Schweizer Alpen. *Schweizerische Mineralogische und Petrographische Mitteilungen*, 41, 335–369.
- Bambauer, von. H.U., Brunner, G.O., and Laves, F. (1962) Wasserstoffgehalte in Quarzen aus Zerrklüften der Schweizer Alpen und die Deutung ihrer regionalen Abhängigkeit. *Schweizerische Mineralogische und Petrographische Mitteilungen*, 42, 221–236.
- (1963) Merkmale des OH-Spektrums alpiner Quarze (3 μ -Gebiet). *Schweizerische Mineralogische und Petrographische Mitteilungen*, 43, 259–268.
- Bottom, V.E. (1953) Final report; Signal Corps contract. In Wenden, 1957, below.
- Cohen, A.J. (1960) Substitutional and interstitial aluminum impurity in quartz, structure and color center interrelationships. *International Journal of the Physics and Chemistry of Solids*, 13, 321–325.
- Curie, J. (1886) In Wenden, 1957, below.
- (1889) Recherches sur la conductibilité des corps cristallisés. *Annales de Chimie et de Physique*, ser. 6, 18, 202–269.
- Dennis, P.F. (1984) Oxygen self-diffusion in quartz under hydrothermal conditions. *Journal of Geophysical Research*, 89, 4047–4057.
- Exner (1901) In Wenden, 1957, below.
- Frischat, G.H. (1969) Tracer diffusion of sodium in the *c*-axis direction of quartz. *Physika Status Solidi*, 35, K47–K49.
- (1970a) Cationic transport in quartz crystals. *Berichte der Deutschen Keramischen Gesellschaft*, 47, 238–243.
- (1970b) Sodium diffusion in natural quartz crystals. *American Ceramic Society Journal*, 53, 357.
- 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.
- Giletti, B.J., and Yund, R.A. (1984) Oxygen diffusion in quartz. *Journal of Geophysical Research*, 89, 4039–4046.
- Glushkova, T.M., and Firsova, M.M. (1968) Electric conductivity of quartz in an alternating electric field. *Soviet Physics—Crystallography*, 12, 871–875.
- Griggs, D.T., and Blacic, J.D. (1965) Quartz: Anomalous weakness of synthetic crystals. *Science*, 147, 292–295.
- Halliburton, L.E., Koumvakalis, N., Markes, M.E., and Martin, J.J. (1981) Radiation effects in crystalline SiO₂: The role of aluminum. *Journal of Applied Physics*, 52, 3565–3574.
- Harris, P.M., and Waring, C.E. (1937) Diffusion of lithium ions through quartz in an electric field. *Journal of Physical Chemistry*, 41, 1077–1085.
- Hirsch, P.B. (1981) Plastic deformation and electronic mechanisms in semiconductors and insulators. *Journal de Physique, Colloque*, 42, (C-3), C3-149–C3-160.
- Hobbs, B. E. (1981) The influence of metamorphic environment upon the deformation of minerals. *Tectonophysics*, 78, 335–383.
- Jain, H., and Nowick, A.S. (1982a) Electrical conductivity of synthetic and natural quartz crystals. *Journal of Applied Physics*, 53, 477–484.
- (1982b) Radiation-induced conductivity in quartz crystals. *Journal of Applied Physics*, 53, 485–489.
- Joffe, A.F. (1928) *The physics of crystals*. McGraw-Hill, New York.
- Kats, A. (1962) Hydrogen in alpha-quartz. *Philips Research Reports*, 17, 1–31, 133–279.
- King, J.C. (1955) Second interim report; Signal Corps contract. In Wenden, 1957, below.
- (1956) Fifth interim report; Signal Corps contract. In Wenden, 1957, below.
- King, J.C., and Sander, H.H. (1972) Rapid annealing of frequency change in crystal resonators following pulsed X-irradiation. *IEEE Transactions Nuclear Science*, NS-19, Dec. 23, 23–32.
- Kreffl, G.B. (1975) Effects of high-temperature electrolysis on the color-

- ation characteristics and OH-absorption bands in alpha-quartz. *Radiation Effects*, 26, 249–259.
- Kronenberg, A.K., Kirby, S.H., Aines, R.D., and Rossman, G.R. (1986) Solubility and diffusional uptake of hydrogen in quartz at high water pressures: Implications for hydrolytic weakening. *Journal of Geophysical Research*, 91, 12723–12744.
- Lopez, A.R., West, J.D., and Martin, J.J. (1986) Electrodiffusion of ions in alpha-quartz. In J.H. Crawford, Jr., Y. Chen, and W.A. Sibley, Eds., *Defect properties and processing of high-technology nonmetallic materials*, Materials Research Society Symposia Proceedings, 24. Elsevier Science Publishing Co., New York.
- Markes, M.E., and Halliburton, L.E. (1979) Defects in synthetic quartz: Radiation-induced mobility of interstitial ions. *Journal of Applied Physics*, 50, 8172–8180.
- Milne, E.L., and Gibbs, P. (1964) Ag ion migration in α -quartz. *Journal of Applied Physics*, 35, 2364–2367.
- Nuttall, R.H.D., and Weil, J.A. (1981) The magnetic properties of the oxygen-hole aluminum centers in crystalline SiO₂. II. (AlO₄/H⁺)⁺ and (AlO₄/Li⁺)⁺. *Canadian Journal of Physics*, 59, 1709–1718.
- Park, D.S., and Nowick, A.S. (1974) Dielectric relaxation of point defects in α -quartz. *Physika Status Solidi, A*, 26, 617–626.
- Rochow, E.G. (1938) Electrical conduction in quartz, periclase, and corundum at low field strength. *Journal of Applied Physics*, 9, 664–669.
- Rybach, L., and Laves, F. (1967) Sodium diffusion experiments in quartz crystals. *Geochimica et Cosmochimica Acta*, 31, 539–546.
- Sarzhevskii, P.E. (1952) *Doklady Adademiia Nauk SSSR*, 82, 571–574 (in Russian). Reviewed by J.M. Hough in *Science Abstracts*, 55.
- Shaffer, E.W., Shi-lan Sang, J., Cooper, A.R., and Heuer, A.H. (1974) Diffusion of tritiated water in β -quartz. In A.W. Hofmann, B.J. Gilletti, H.S. Yoder, Jr., and R.A. Yund, Eds., *Geochemical transport and kinetics*. Carnegie Institution of Washington Publication 634, 131–138.
- Shewmon, P.G. (1963) *Diffusion in solids*. McGraw-Hill, New York.
- Snow, E.H., and Gibbs, P. (1964) Dielectric loss due to impurity cation migration in alpha-quartz. *Journal of Applied Physics*, 35, 2368–2374.
- Stevens, J.M., and Volger, J. (1962) Further experimental investigation on the dielectric losses of quartz crystals in relation to their imperfections. *Philips Research Reports*, 17, 283–314.
- Strauss, S.W., et al. (1956) Fundamental factors controlling electrical resistivity in vitreous ternary lead silicates. *Journal of Research of National Bureau of Standards*, 56, 135–142. In Wenden, 1957, below.
- Stuart, M.R. (1955) Dielectric constant of quartz as a function of frequency and temperature. *Journal of Applied Physics*, 26, 1399–1404.
- Sykes, A.G., and Weil, J.A. (1970) The formation, structure, and reactions of binuclear complexes of cobalt. In J.O. Edwards, Ed., *Progress in inorganic chemistry*, 13, p. 1–106. Interscience Publishers, New York.
- Vogel, R.C., and Gibson, G. (1950) Migration of sodium ions through quartz plates in an electric field I. *Journal of Chemical Physics*, 18, 490–494.
- Verhoogen, J. (1952) Ionic diffusion and electrical conductivity in quartz. *American Mineralogist*, 37, 637–655.
- Warburg, E., and Tegetmeier, F. (1887) In Wenden, 1957, below.
- (1888) Ueber die electrolytische Leitung des Bergkrystalls. *Annalen der Physik und Chemie*, 35, 455–467.
- Weil, J.A. (1975) The aluminum centers in alpha-quartz. *Radiation Effects*, 26, 261–265.
- Wenden, H.E. (1957) Ionic diffusion and the properties of quartz, I. The direct current resistivity. *American Mineralogist*, 42, 859–888.
- White, S. (1970) Ionic diffusion in quartz. *Nature*, 225, 375–376.
- (1971) Hydroxyl ion diffusion in quartz. *Nature Physical Science*, 230, 192.

MANUSCRIPT RECEIVED OCTOBER 13, 1986

MANUSCRIPT ACCEPTED MARCH 23, 1987