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TOPAZ: ENERGY CALCULATIONS BEARING ON THE LOCATION OF HYDROGEN

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ABSTRACT

Energy calculations are used to address two problems related to reduced symmetry in OH-bearing topaz, (1) the influence of different local orderings of OH and F on the location of a hydrogen atom, and (2) the relative stability of an H^+ ion in differently ordered local environments. The purpose was to test an H–H avoidance rule and scheme of hydrogen bonding proposed by Parise (1980, Parise *et al.* 1980), and to test the hypothesis, based on infrared absorption data (Aines & Rossman 1986), that there are two kinds of hydrogen sites in topaz. The calculations involved a search for the position of minimum energy for an H^+ ion in a local environment of 35 to 40 neighboring atoms. The results fall into three groups, distinguished by calculated hydrogen positions and energies. Group I consists of local OH–F orderings in which the hydrogen position is neither stabilized nor destabilized by hydrogen bonding, and not influenced by relatively short-range H–H repulsion (H–H < 2 Å). Calculated group-I energies are low, and the positions are consistent with observed positions of the hydrogen. Group II consists of local OH–F orderings in which H–H repulsion is significant. Hydrogen energies are very high; thus the group-II orderings are probably not important in natural topaz. Group III consists of local OH–F orderings in which hydrogen is stabilized by hydrogen bonding. The calculated energies are low, and the hydrogen positions may correspond to the second kind of hydrogen site indicated by infrared absorption data.

Keywords: topaz, hydroxyl, short-range order, energy calculations.

SOMMAIRE

Les calculs des niveaux d'énergie interne de la topaze servent à adresser deux problèmes concernant la réduction en symétrie d'échantillons riches en OH: 1) l'influence qu'ont les agencements localement ordonnés de OH et de F sur le site favorisé par un atome d'hydrogène, et 2) la stabilité relative d'un ion H^+ dans des milieux différemment ordonnés. Il s'agissait de vérifier la règle de l'évitement des liaisons H–H et le schéma des liaisons de l'hydrogène qu'avaient proposés Parise (1980) et Parise *et al.* (1980), et l'hypothèse de Aines et Rossman (1986), fondée sur les données d'absorption infra-rouge, qu'il y a deux sortes de sites de l'hydrogène dans la topaze. Les calculs impliquent la détermination de la position d'un ion de H^+ ayant une énergie minimum dans un groupement de 35 à 40 atomes. Les résultats définissent trois groupes de positions calculées et de niveaux d'énergie. Le groupe I comprend les regroupements locaux de OH et de F dans lesquels la position de l'ion H^+ est ni stabilisée, ni déstabilisée par la liaison de l'hydrogène, et non influencée par la répulsion H–H à relativement courte distance entre deux ions de H^+ (<2 Å). Les énergies calculées pour le groupe I sont faibles, et les positions concordent avec les positions observées. Les solutions du groupe II se rapportent aux groupements ordonnés locaux de OH et de F dans lesquels la répulsion H–H est importante. Les énergies de l'hydrogène sont très élevées; les solutions du groupe II ne seraient donc pas importantes dans la topaze naturelle. Dans les solutions du groupe III, les regroupements ordonnés de OH et de F contiennent de l'hydrogène stabilisé par la présence de liaisons de l'hydrogène. Les énergies calculées dans ce cas sont faibles, et les positions de l'hydrogène pourraient correspondre à la deuxième catégorie de sites de l'hydrogène, telles qu'indiquée par les spectres d'absorption infra-rouge.

(Traduit par la Rédaction)

Mots-clés: topaze, hydroxyle, ordre atomique local, calculs d'énergie.

INTRODUCTION

The major mechanism of solid solution in topaz involves the substitution of hydroxyl for fluorine, OHF_{-1}, but in natural samples of topaz the fraction OH/(F + OH) does not exceed approximately 0.30 (Rosenberg 1967, Ribbe & Rosenberg 1971, Ribbe 1982). Pure F-topaz and most OH-bearing topaz are orthorhombic, space group *Pbnm* (Ribbe 1982). In orthorhombic topaz, all hydrogen sites, 8 per unit cell, are symmetrically equivalent, and thus OH and F are necessarily disordered. However, the optical properties of OH-bearing topaz are not always consistent with an orthorhombic symmetry. In a detailed study of the optical properties of two crystals of OH-bearing topaz, Akizuki *et al.* (1979) showed that depending on the direction of growth, certain sectors are monoclinic or triclinic. After heating to 950°C, the low-symmetry sectors became orthorhombic. Akizuki *et al.* (1979) proposed that the low symmetry of the monoclinic and triclinic sectors is due to the ordering of OH and F.

Using neutron-diffraction data, Zemann *et al.* (1979) and Parise *et al.* (1980) determined nearly the same location for hydrogen atoms in topaz referred

to space group *Pbnm* (Table 1, Figs. 1, 2). The fraction OH/(F + OH) was reported as 0.28 and 0.09, respectively, for the crystals used by Zemann *et al.* (1979) and Parise *et al.* (1980). In space group *Pbnm*, the partial occupancy of each hydrogen site would correspond to the bulk value of OH/(F + OH). Refinement of the structure in space group *P*1 (Parise *et al.* 1980, Parise 1980) gave a single hydrogen site in nearly the same location as one of the eight equivalent sites determined in *Pbnm* (Table 1, Fig. 2). The partial occupancy of the single hydrogen site would be eight times the bulk fraction of OH/(F + OH), or approximately 0.72 in the topaz examined by Parise

TABLE 1. OBSERVED HYDROGEN LOCATIONS IN TOPAZ

	Space group	x	y	z
Zemann et al. (1979)[1]	Pbnm	0.4973	0.2508	0.162
Parise (1980)[2,3]	P1	0.498	0.254	0.161
Parise et al. (1980)[2]	Pbnm	0.494	0.253	0.161
Parise et al. (1980)[2]	P1	0.500	0.250	0.170

1. a = 4.6651 Å, b = 8.8028 Å, c = 8.3904 Å.
2. a = 4.6520 Å, b = 8.8028 Å, $\alpha=\beta=\gamma=90°$.
3. reported in Ribbe (1982).

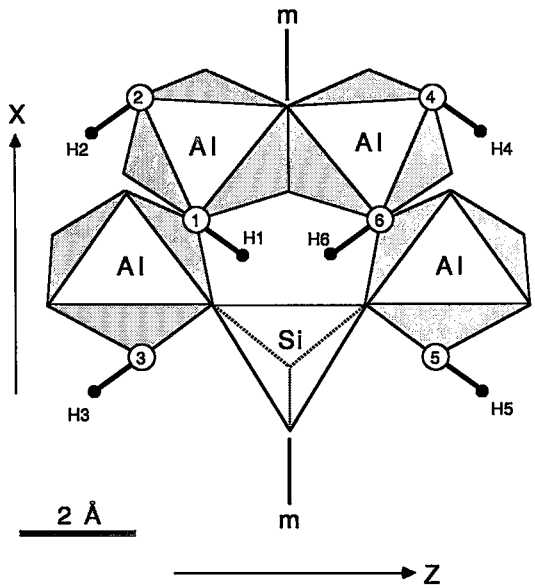

FIG. 1. Part of the structure of topaz projected down the *b* axis, onto the (0 1 0) plane. Numbered open circles are fluorine or hydroxyl oxygen sites (F1, F2, F3, F4, F5, F6 sites). Other vertices of the Al octahedra and Si tetrahedron are occupied by non-hydroxyl oxygen atoms. Positions for the anions are based on the structure determination by Ladell (1965). Positions for hydrogen atoms (small filled circles, H1...H6) are from Parise *et al.* (1980).

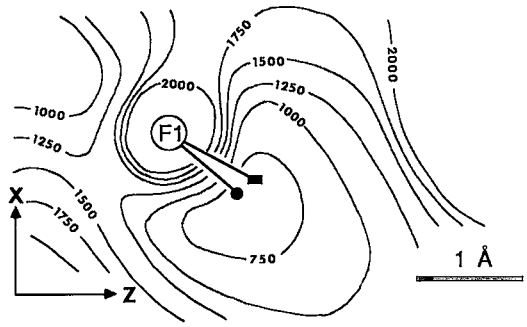

FIG. 2. Map of the H1 hydrogen energy, W_H, in the (0 1 0) plane passing through the F1 oxygen. The energy contours (kJ/mole of H^+) pertain to OH–F ordering #1 in Table 2. The small, filled circle marks the location of the calculated energy-minimum. Observed hydrogen sites (Table 1) are all contained in the small, filled rectangle. Energies for the map were computed by the program QUICKMAP.

et al. (1980). The ideal *P*1 structure would be saturated with hydroxyl (*i.e.*, no vacant hydrogen sites) when the bulk fraction of OH/(F + OH) is 1/8. Thus topaz with a higher OH/(F + OH) fraction, such as for the topaz examined by Zemann *et al.* (1979), must have either greater symmetry than *P*1 or more than one kind of hydrogen site in *P*1. Parise *et al.* (1980) noted that in the space group *Pbnm*, hydrogen atoms on adjacent sites related by the (0 0 1) mirror would be uncomfortably close together, the H–H distance being 1.5 Å, and that avoidance of the H–H repulsion in such a situation could in part be responsible for OH–F ordering in space group *P*1. Parise (1980, cited in Ribbe 1982) also noted that hydrogen bonding, O–H...O or O–H...F, may be important in stabilizing hydrogen in the structure, insofar as two H...O distances and one H...F distance are relatively short (2.28 Å, 2.29 Å, 2.39 Å, respectively).

Infrared absorption data (Aines & Rossman 1986) show evidence for two kinds of hydrogen sites, one of which is consistent with observed positions (Table 1). Aines & Rossman (1986) suggested that one hydrogen atom of a pair otherwise related by the (0 0 1) mirror in *Pbnm* might be deflected, hence creating a second kind of site.

In the work presented in this paper, energy calculations were used to address two problems related to reduced symmetry in topaz, (1) the influence of different local orderings of OH and F on the location of a hydrogen atom, and (2) the relative stability of hydrogen atoms in differently ordered local environments. The purpose is to test Parise's H–H avoidance rule (Parise *et al.* 1980) and scheme of hydrogen bonding (Parise 1980, see Ribbe 1982) and to test the hypothesis of Aines & Rossman (1986) that there are two kinds of hydrogen sites.

Structure of Topaz

The energy calculations were performed on Ladell's (1965) structure determination, details of which are described by Ribbe & Gibbs (1971). The space group is *Pbnm*. No site was determined for the small amount of hydrogen [OH/(F + OH) < 0.05]. Figure 1 shows a projection of the structure onto the (0 1 0) plane, with hydrogen positions consistent with the determinations reported in Table 1. The structure consists of close-packed anions (O, F), with a stacking sequence ABAC in the Y direction. One-third of the octahedral sites are occupied by Al, and one-twelfth of the tetrahedral sites are occupied by Si. The "A" anion sheets of the stacking sequence are made up of hydroxyl oxygen, fluorine, and non-hydroxyl oxygen in the ratio (OH+F):O = 2:1. The sheets of "B" and "C" anions are made up of non-hydroxyl oxygen atoms only. The OH dipoles lie approximately in the planes of the "A" sheets. For the purposes of this paper, otherwise symmetrically equivalent fluorine or hydroxyl oxygen sites will be referred to as F1, F2, F3, F4, F5 and F6. These anion sites are labeled by number in Figure 1. Where oxygen is substituted for fluorine on one of the sites (*e.g.*, O on site F3), the corresponding hydrogen atom will be referred to by the same number (*i.e.*, the H3 hydrogen). All of the energy calculations were performed on the H1 hydrogen near an oxygen atom at the F1 site. In space group *Pbnm*, the H2 and H3 hydrogen sites are related to the H1 site by a 2_1 screw axis parallel to [1 0 0]. The H4 and H5 hydrogen sites are related to the H1 site by a (0 1 0) *n*-glide plane. The H6 site is related to the H1 site by the (0 0 1) mirror.

Method

The energy calculations follow the method of Abbott *et al.* (1989a, b). In the present context, the procedure involves a search for the position of lowest energy for a proton (H1 hydrogen) near an oxygen atom at the F1 site. The energy was calculated according to

$$W_H = \Sigma_i [(k \cdot q_H \cdot q_i / r_{iH}) + \lambda_{iH} \exp(-r_{iH}/\rho_{iH})],$$

where the summation is made over a finite set of neighboring atoms i. The first term in the square brackets refers to the Coulombic energy, where q_H and q_i are electrostatic charges, r_{iH} is the i–H interatomic distance, and the constant k converts units of $e^2/Å$ to kJ. The second term in the square brackets refers to the short-range repulsion between H and atom i. For the short-range repulsion between oxygen and hydrogen, Abbott *et al.* (1989a, b) determined λ_{OH} and ρ_{OH} values empirically, 30000 kJ/mole of H^+ and 0.25 Å, respectively, in such a way that they are consistent with formal ionic charges in the Coulombic term (*i.e.*, $q_O = -2$, $q_H = 1$, *etc.*). The values work well in a wide range of structures, provided the ionic potential of the hydroxyl oxygen is close to 2 e/Å. None of the F–H distances, observed or calculated, were found to be shorter than 2.19 Å. By analogy with the behavior of the O–H pair, for such distances short-range F–H repulsions would be negligible; hence, precise values for λ_{FH} and ρ_{FH} are not crucial. For the purposes of the calculations, λ_{FH} was set equal to ρ_{OH} (30000 kJ/mole of H^+), and ρ_{FH} was set equal to ρ_{OH} (0.25 Å). For relevant H–H, H–Si, and H–Al distances, the short-range repulsions are negligible. In order to simplify the calculations, such short-range terms were omitted by setting $\lambda_{H\text{-}Si} = \lambda_{H\text{-}Al} = \lambda_{H\text{-}H} = 0$.

The calculations were performed on a discrete 40-site cluster, which was selected on the basis of two criteria. (1) For a charge distribution consistent with the observed *P*1 structure (case 1, Table 2), the cluster must yield a calculated position of the hydrogen atom close to the observed position (Table 1). (2) There must be sufficient F-sites to address relevant local orderings of F and OH (sites F1 to F6, Fig. 1). Beyond these constraints, the exact number of sites in the cluster is not important, because the purpose of the calculations is simply to determine relative changes in the position of a selected hydrogen atom as a function of variations in the distribution of OH and F in the immediate surroundings (*i.e.*, variations in local, or short-range, order of OH and F). Depending on the number of OHF_{-1} exchanges involved in a given local ordering, from 35 to 40 of the cluster sites were occupied. Neighboring atoms included 22 anions (0–5 F, 22–17 O), 5 Si, 8 Al, and up to 5 H (H2, H3, H4, H5, H6 in Fig. 1). That the cluster has a net charge is not important because the net charge (+6) is the same in all of the calculations, in strict accordance with the OHF_{-1} exchange. The unit-cell geometry and positions for Si, Al, O and F were taken from the structure determination by Ladell (1965). Observed positions for the H1 hydrogen (Table 1) are near the center of the 40-site cluster, such that in any given local ordering of OH and F the neighboring atoms were within a radius of approximately 5.25 Å.

The present approach, which involves only a small volume of the structure, was adopted in order to avoid certain problems with alternative methods, specifically methods that involve the calculation of the total cohesive energy (Appendix) by means of any variant of the Ewald–Bertaut–Williams procedure (*e.g.*, Busing 1981). Such methods work only for perfectly ordered, periodic structures. In topaz, for example, a specific local ordering of OH and F in one unit cell would be repeated periodically throughout the extended structure. Short-range ordering, commonly manifested in long-range disordering, cannot be accommodated satisfactorily. The Appen-

dix gives a brief account of the method applied to local ordering #1 (Table 2). This OH–F ordering corresponds to the only structure determination of a well-ordered OH-bearing topaz (Parise 1980, Parise *et al.* 1980). The calculated position of the hydrogen atom [0.495, 0.244, 0.161] is very close to the observed positions (Table 1), and not much different from the position calculated on the basis of the calculation for a simpler cluster (#1, Table 2).

Of course, in the real local environments of hydrogen in topaz, the positions of all the nearby atoms (O, F, Al, Si, other H) would depend on the local ordering of OH and F (Ribbe 1982). At present, such effects cannot be treated realistically, but in topaz there are two indications that the effect is probably small. (1) The very small thermal vibration parameters determined by Ladell (1965) for O, F, Al and Si in *Pbnm* topaz admit only a small extent of positional disordering. (2) Ribbe (1982) indicated that the local environments of the monovalent anions (1"OH" + 7 F environments) in *P*1 topaz are very similar.

In the 35- to 40-atom clusters used in this study, there are six nearest-neighbor fluorine or hydroxyl oxygen sites (F1...F6 in Fig. 1). A –2 charge (oxygen) was placed at the F1 site. The calculations were then performed on each of the 32 possible combinations of –1 charges (fluorine) and –2 charges (oxygen) on sites F2, F3, F4, F5 and F6 (Table 2). For clusters involving oxygen atoms on one or more of these sites (all but one of the 32 orderings), a hydrogen atom was included in the set of neighboring atoms for each substituted oxygen atom, in accordance with the exchange OHF_{-1} (maintaining the same net charge on the cluster). Each neighboring H2, H3, H4, H5 or H6 hydrogen was positioned with respect to the H1 hydrogen according to the appropriate element of symmetry of *Pbnm*. During the search for a minimum-energy configuration, the position of each neighboring H2, H3, H4, H5 or H6 hydrogen was adjusted so as to maintain the symmetrical relationship to the H1 hydrogen. For example, local OH–F ordering #6 in Table 2 involves oxygen at the F6 site. During the search for the position of minimum energy for the H1 hydrogen, the H6 hydrogen was maintained at a position that is symmetrically related by the (0 0 1) mirror to the changing position of the H1 hydrogen. In this particular case, the H1–H6 distance changed from an initial, observed distance of 1.5 Å to a final, more reasonable distance of 2.28 Å. Also, for ordering #6 (Table 2), attempts to search for an asymmetrical pair of H1 and H6 hydrogen positions all terminated at the same minimum-energy configuration in which the H1 and H6 hydrogen atoms were related by the (0 0 1) mirror.

The calculations were done using the computer programs QUICKSIT and QUICKMAP. In QUICKSIT, the search procedure employs the modified simplex method (Cooper 1981). The programs were written in PASCAL, and are available from the author for MacIntosh or IBM-compatible personal computers.

TABLE 2. CALCULATED HYDROGEN LOCATIONS IN TOPAZ[1]

	Charges on F sites						H1-site			W_H	H1-H6	H1-F3
	F1	F2	F3	F4	F5	F6	x	y	z	(kJ)	(Å)	(Å)
1	-2	-1	-1	-1	-1	-1	0.461	0.221	0.143	663	--	2.40
2	-2	-2	-1	-1	-1	-1	0.475	0.225	0.150	656	--	2.48
3	-2	-1	-2	-1	-1	-1	0.419	0.190	0.085	476	--	1.98
4	-2	-1	-1	-2	-1	-1	0.467	0.222	0.145	646	--	2.42
5	-2	-1	-1	-1	-2	-1	0.467	0.225	0.148	591	--	2.43
6	-2	-1	-1	-1	-1	-2	0.444	0.203	0.116	801	2.28	2.20
7	-2	-2	-2	-1	-1	-1	0.421	0.191	0.094	533	--	2.03
8	-2	-2	-1	-2	-1	-1	0.481	0.256	0.152	628	--	2.51
9	-2	-2	-1	-1	-2	-1	0.480	0.232	0.161	573	--	2.55
10	-2	-2	-1	-1	-1	-2	0.451	0.206	0.122	842	2.18	2.25
11	-2	-1	-2	-2	-1	-1	0.420	0.187	0.081	489	--	1.96
12	-2	-1	-2	-1	-2	-1	0.421	0.197	0.098	424	--	2.03
13	-2	-1	-2	-1	-1	-2	0.421	0.186	0.074	528	2.95	1.94
14	-2	-1	-1	-2	-2	-1	0.471	0.225	0.149	571	--	2.46
15	-2	-1	-1	-2	-1	-2	0.444	0.199	0.112	796	2.32	2.19
16	-2	-1	-1	-1	-2	-2	0.446	0.206	0.120	759	2.18	2.23
17	-2	-1	-1	-2	-2	-2	0.446	0.203	0.118	752	2.21	2.22
18	-2	-1	-2	-1	-2	-2	0.422	0.188	0.081	495	2.84	1.97
19	-2	-1	-2	-2	-1	-2	0.422	0.184	0.072	539	2.99	1.94
20	-2	-1	-2	-2	-2	-1	0.421	0.192	0.091	436	--	2.01
21	-2	-2	-1	-1	-2	-2	0.450	0.206	0.124	793	2.10	2.26
22	-2	-2	-1	-2	-1	-2	0.449	0.198	0.115	830	2.26	2.22
23	-2	-2	-1	-2	-2	-1	0.484	0.288	0.155	550	--	2.53
24	-2	-2	-2	-1	-1	-2	0.422	0.184	0.078	599	2.88	1.97
25	-2	-2	-2	-1	-2	-1	0.427	0.203	0.113	480	--	2.13
26	-2	-2	-2	-2	-1	-1	0.422	0.188	0.087	546	--	2.00
27	-2	-1	-2	-2	-2	-2	0.423	0.186	0.077	504	2.90	1.96
28	-2	-2	-1	-2	-2	-2	0.452	0.205	0.124	782	2.11	2.27
29	-2	-2	-2	-1	-2	-2	0.423	0.187	0.085	561	2.77	2.00
30	-2	-2	-2	-2	-1	-2	0.424	0.181	0.075	606	2.93	1.97
31	-2	-2	-2	-2	-2	-1	0.426	0.197	0.106	471	--	2.09
32	-2	-2	-2	-2	-2	-2	0.424	0.184	0.081	568	2.84	1.99

1. referred to structure determination by Ladell (1965): Pbnm, a = 4.6499 Å, b = 8.7968 Å, c = 8.3909 Å.

Results and Discussion

For an H1 hydrogen atom, near an oxygen atom at the F1 site, Table 2 gives the coordinates and energy, W_H, at the position of minimum energy for each of the 32 possible orderings of oxygen and fluorine on sites F2, F3, F4, F5 and F6 (Fig. 1). The table also gives interatomic distances H1–F3 and, where relevant, H1–H6.

The simplest ordering involves fluorine atoms at F2, F3, F4, F5 and F6 (*i.e.*, no OHF_{-1} substitution in the local environment surrounding the F1–H1 oxygen–hydrogen pair). Presumably this situation would pertain to a low ratio OH/(F + OH), where the hydroxyl groups are more or less evenly distributed over the extended structure. The ordering approximates the local environment of a hydroxyl group in the *P*1 structure (Parise 1980, Parise *et al.* 1980). Figure 2 is a map of the energy, W_H, that a hydrogen atom would have at different positions in the (0 1 0) plane passing through the F1 oxygen atom. All of the observed positions of hydrogen (Table 1) plot in the small, filled rectangle. The calculated minimum-energy position (ordering #1, Table 2) is marked by the filled circle. The calculated and observed positions are approximately 0.4 Å apart. The calculated H1–F1 distance is 0.99 Å, which is

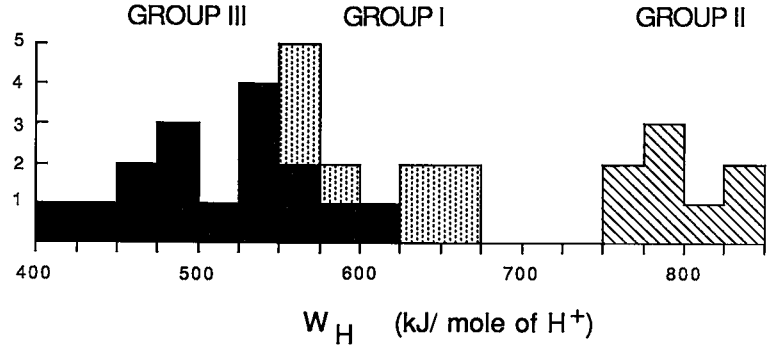

FIG. 3. Histogram of calculated minimum energies in Table 2.

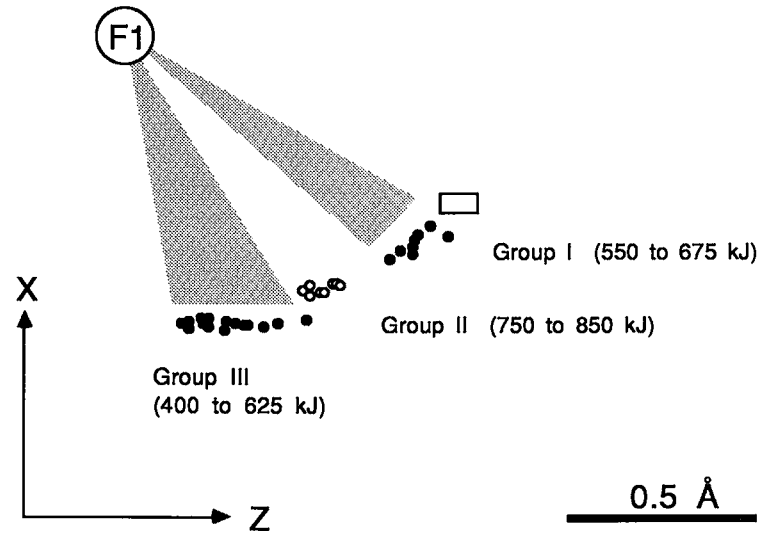

FIG. 4. The locations of the calculated energy-minima (Table 2), projected onto the (0 1 0) plane passing through the F1 oxygen. Observed hydrogen positions (Table 1) plot in the rectangle.

only slightly longer than the observed distance of 0.97 Å (Parise 1980, in Ribbe 1982). The calculated and observed angles *a*–F1–H1, 115° and 134° respectively, differ by 19°. *For purposes of comparison of the effects of different OH–F orderings, this discrepancy between calculated and observed OH orientations is acceptable. The reader should, however, keep in mind that OH dipoles, based on the calculated positions (Table 2) may all be systematically misoriented by as much as 20°.*

The results reported in Table 2 fall into three groups, which are distinguished on the basis of the calculated energies (Fig. 3) and the calculated location of the H1 hydrogen (Fig. 4). Group I consists of all OH–F orderings involving ±H2 ±H4 ±H5 hydrogen atoms (*i.e.*, all orderings with no H3 hydrogen and no H6 hydrogen). This includes the simplest ordering just discussed, ordering #1 (Fig. 2, Table 2), which is fairly representative of the group. Energies in Group I range from 550 to 675 kJ/mole of H^+ (Fig. 3). The calculated locations for the H1 hydrogen are reasonably close to the observed positions (Table 1). The results indicate that any combination of H2, H4 and H5 hydrogen atoms has little influence on the location of the H1 hydrogen, and little influence on the energy.

Group II consists of all orderings involving H6 ± H2 ± H4 ± H5 hydrogen atoms (*i.e.*, orderings with an H6 hydrogen, but no H3 hydrogen). This group includes the simplest violation of the H–H avoidance rule, ordering #6 (Table 2), which is fairly representative of the group. The distinguishing characteris-

tics of the group-II orderings may be attributed to the effects of repulsion between two closely juxtaposed H1 and H6 hydrogen atoms. The repulsion between H1 and H6 hydrogen atoms causes the corresponding OH dipoles to rotate away from each other, widening the angles *a*-F1-H1 and *a*-F6-H6 (Fig. 4), thus increasing the H1-H6 distance. Group-II orderings have the highest energies, from 750 to 850 kJ/mole of H^+, which supports the H-H avoidance rule. With such high energies, group-II local orderings are probably not very important in natural topaz.

Group III includes any ordering involving an H3 hydrogen (*i.e.*, H3 ± H2 ± H4 ± H5 ± H6 hydrogen atoms). The simplest ordering in the group is #3 in Table 2. Like groups I and II, the simplest ordering is fairly representative of the group, and the group characteristics are not influenced significantly by the presence or absence of any combination of H2, H4 and H5 hydrogen atoms. However, the influence of an H6 hydrogen atom appears not to be so clear as it was in group II, primarily because the group-III energies are by far the lowest, from 400 to 625 kJ/mole of H^+ (Fig. 3). Group-III orderings involving an H6 hydrogen have the longest H1-H6 distances, 2.77 to 2.99 Å (Table 2), which might be attributed to H-H repulsion, but the angles *a*-F1-H1 in the group are similarly wide regardless of the presence or absence of an H6 hydrogen (Fig. 4). Of more significance in explaining the characteristics of the group are the unusually short H1-F3 distances, from 1.94 to 2.13 Å (Table 2). The shortened H1-F3 distances are attributable to the attraction of the F3 oxygen. Evidently the group-III orderings are stabilized by hydrogen bonding of the sort O_{F1}-H_{H1}...O_{F3}. It should be noted that *within* group III, orderings involving an H6 hydrogen do have the highest energies, but the energies are still significantly lower than any of the group-II energy levels. Thus the most important feature of group III is the hydrogen bonding, inferred on the basis of the short, calculated O_{F3}...H distances (Table 2). With their relatively low energies, group-III local orderings could be very important in natural samples of topaz, and provide a possible explanation for the infrared absorption data (Aines & Rossman 1986), which indicate two kinds of hydrogen sites. In low-symmetry topaz, *e.g.*, in space group *P*1, excess hydrogen over the amount consistent with an OH/(F + OH) fraction of 1/8 may be accommodated in sites stabilized by hydrogen bonding.

Conclusions

1. Local orderings consistent with group I are neither stabilized by hydrogen bonding, nor destabilized by H-H repulsion. The energies are low, and the calculated positions for the H1 hydrogen are consistent with observed positions. Thus any combination of neighboring H2, H4 and H5 hydrogen atoms has little influence on the energy and position of the H1 hydrogen. For very low fractions of OH/(F + OH), which is the case in most samples of topaz, entropy considerations may dictate that group-I local orderings are more important than group-III local orderings, even though the latter have somewhat lower calculated energies.

2. The H-H avoidance principle (Parise *et al.* 1980) does not pertain to all local OH-F orderings involving hydrogen atoms related by the (0 0 1) mirror. The principle is relevant only in local orderings that preclude hydrogen bonding of the sort O_F-H_{H1}...O_{F3}. Local orderings subject to the destabilizing influence of H-H repulsion, as in group II (H6 ± H2 ± H4 ± H5), have high energies and are probably not very important in natural topaz.

3. Hydrogen bonding of the sort O_{F1}-H_{H1}...O_{F3} in group-III orderings (H3 ± H2 ± H4 ± H5 ± H6) stabilizes the structure regardless of the presence or absence of other hydrogen atoms. Hydrogen sites stabilized by hydrogen bonding may account for infrared absorption data that indicate two kinds of hydrogen sites in topaz.

With regard to hydrogen bonding, it is tempting to consider an extended chain of oxygen atoms substituting for each of the fluorine atoms adjacent to a particular [1 0 0] 2_1 screw axis. The associated hydrogen atoms would be in symmetrically equivalent local environments like the H1 environment in group-III ordering #7 (-2 charges at F1, F2 and F3 in Table 2). Such a linear defect of hydroxyl groups should be stabilized along its length by hydrogen bonding. By further extension, and by analogy with the synthesis of pure OH-chondrodite (Yamamoto 1977), where a similar problem exists, it may even be possible to synthesize pure OH-topaz at high pressures. This is suggested by the relatively low energy for the group-III ordering involving hydroxyl substituted for all the fluorine atoms (ordering #32, Table 2).

Note added in proof:

Regarding the last conclusion, a pure OH-topaz recently has been synthesized at high pressure by Medenbach *et al.* (1990).

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APPENDIX

Additional calculations of energy were performed using the computer program WMIN (Busing 1981). This is a mainframe computer operation, as opposed to the simple calculation of the hydrogen energy in a 35- or 40-atom cluster, which can be done conveniently on either a MacIntosh or an IBM-compatible PC with as little as 256 k RAM. The WMIN calculations were designed to search for the minimum-energy position for hydrogen in a perfectly ordered topaz of composition $Al_8Si_4O_{16}F_7(OH)$. The ordering of the hydroxyl oxygen atom and 7 fluorine atoms was consistent with the *P*1 structure determination of Parise *et al.* (1980, Parise 1980). This corresponds to OH–F ordering #1 in Table 2. Atomic coordinates for Al, Si, O and F were taken from the *Pbnm* structure determination of Ladell (1965). Thus, except for the hydrogen atom and the distribution of –1 (F) and –2 (O) charges, the structure would be in space group *Pbnm*. The positions of all Al, Si, O and F atoms were fixed during the search procedure. Only the position of the hydrogen atom was allowed to vary.

The total cohesive energy (Post & Burnham 1986) is given by:

$$W_{tot} = 1/2k\Sigma_{i\neq j}\,\Sigma_j\, q_i q_j/r_{ij} + 1/2\,\Sigma_{i\neq j}\Sigma_j\,\lambda_{ij}\exp(-r_{ij}/\rho_{ij}).$$

The first summation includes the Coulombic terms, where q_i and q_j are ionic charges on atom i and j, r_{ij} is the interatomic distance, and k is a constant of proportionality. The second summation includes the short-range repulsion terms (Post & Burnham 1986). For the purpose of calculating the minimum-energy position for H, with the positions of all other atoms fixed, only the short-range coefficients λ_{OH}, λ_{FH}, ρ_{OH} and ρ_{FH} are relevant. For these, the same values were used as in the cluster calculations, $\lambda_{OH} = \lambda_{FH} = 30000$ kJ and $\rho_{OH} = \rho_{FH} = 0.25$ Å. All other short-range interactions were omitted from the summation by setting all relevant λ_{ij} equal to 0. The final cohesive energy W_{tot} is equal to –4611.0 kJ/mole of anions, and the minimum-energy hydrogen position is [0.495, 0.244, 0.161]. The reader should note that the formulation of the total cohesive-energy, W_{tot}, and the formulation of the hydrogen energy in a cluster, W_H, are very different; hence, the two cannot be compared in any rational way.