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Modeling tunnel-cation displacements in hollandites using structure-energy calculations

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ABSTRACT

Structure-energy calculations show that the minimum-energy positions of tunnel cations in hollandite compounds and minerals are a function of the configuration of the lower-valence cations in the octahedral sites. The narrow range of energies calculated for many of the configurations suggests that the octahedral cations are probably disordered. Consequently, if a hollandite crystal contains a variety of arrangements of octahedral cations in different unit cells, there will be a corresponding range of tunnel-cation positions giving rise to the positional disorder observed for the tunnel-cation sites in X-ray structure refinements. Calculated Ba and K tunnel-cation distributions for hollandite structures with tunnel sites one-half and two-thirds filled compare quite well with observed tunnel-site electron-density distributions.

INTRODUCTION

One of the important applications of structure-energy calculations of minerals is to assist the interpretation of certain details of X-ray structure refinements, particularly cases involving short-range order and positional disorder. For example, a structure refinement might reveal an anomalously large temperature factor for a given atom; positional disorder then is indicated for that atom, but because of limitations on the resolution of the refinement and because the refinement describes an average unit cell, the exact cause of the disorder usually remains speculative. Likewise, structure refinements do not provide exact information about short-range order in minerals. In cases like these, it is sometimes possible, using structure-energy calculations, to model a variety of ordering or substitution schemes to determine the most likely cause of the positional disorder, or to ascertain whether short-range ordering of certain atoms is energetically favorable. In some previous studies, structure-energy calculations have been used to investigate short-range ordering of Ta and Nb in columbite (Giese, 1975) and to model Na positions in albite (Brown and Fenn, 1979; Post and Burnham, 1984). Also, J. A. Docka, J. E. Post, D. L. Bish, and C. W. Burnham (unpub. ms.) have examined the effects of a variety of substitutions on the A cation position in some amphiboles, and Chamberlain et al. (1985) determined that short-range ordering of Cl^- and CO_3^{2-} in scapolite is energetically favorable and therefore could give rise to antiphase domains in intermediate scapolites. Similar studies have concentrated on (Al,Si) ordering in pyroxenes (Cohen and Burnham, 1985) and micas (Abbott, 1984).

Structure refinements of several hollandite minerals and compounds show that their tunnel cations exhibit positional disorder (e.g., Sinclair et al., 1980; Post et al., 1982). We have used structure-energy calculations incorporating short-range (repulsive) energy parameters derived from the modified electron-gas (MEG) theory to study these structures in an effort to gain insights into the nature of this positional disorder.

Hollandite-structure materials have the general formula $A_{0-2}B_8O_{16}$. Their structures consists of double chains of edge-sharing B–O octahedra that corner-share with other double chains to form a framework containing large tunnels parallel to the tetragonal **c** or monoclinic **b** axis (Fig. 1). The tunnels are partially filled with large monovalent or divalent A cations such as Ba^{2+}, Sr^{2+}, Pb^{2+}, K^+, or Na^+, and the octahedral sites are occupied by a combination of tetravalent and lower-charged cations including Mn^{4+}, Ti^{4+}, Al^{3+}, Fe^{3+}, Mg^{2+}, etc. Lower-valence ($<+4$) B cations are essential to offset the positive charge of the tunnel cations. Minerals with the hollandite structure have either Mn^{4+} or Ti^{4+} as the major B cation. The Mn phases include cryptomelane (A cation = K), hollandite (A = Ba), coronadite (A = Pb), and manjiroite (A = Na), and their Ti^{4+} analogues are priderite (A = K,Ba) and retledgite (A = Ba). Also, there exist a large number of synthetic hollandite-type compounds having a variety of compositions.

In the ideal $I4/m$ hollandite structure, the A cations occupy special position 2a at (0,0,0). Hollandite minerals with divalent A cations generally have tunnel-site occupancies near 0.5 (i.e., one tunnel cation per unit cell), but in hollandites with Na and/or K as the major tunnel cations, the 2a sites are usually two-thirds to three-quarters filled. Hollandite compounds have been synthesized that have tunnel-site occupancies ranging from 0.33 to 1.0.

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Single-crystal X-ray and neutron refinements of hollandite phases show that in some cases the A cations are displaced off the special position along the tunnel direction. For example, Sinclair et al. (1980) observed the Ba in $(Ba_{0.98}Ca_{0.03})(Ti_{6.4}Al_{1.1}Ni_{0.48}Zr_{0.02})O_{16}$ to be displaced 0.6 Å, and Post et al. (1982) reported displacements of a portion of the tunnel cations in hollandite, cryptomelane, and priderite. Structure refinements typically show anomalously large apparent thermal motion associated with the A cations, especially parallel to the tunnel direction (e.g., Cadee and Verschoor, 1978; Sinclair et al., 1980; Post et al., 1982). Root-mean-square displacements in the tunnel direction range from 0.2 to 0.3 Å. These large apparent temperature factors and the split A sites observed by Post et al. (1982) suggest the presence of positional disorder, the exact nature of which has not been previously investigated in detail.

In their study of $(Ba_{0.98}Ca_{0.03})(Ti_{6.4}Al_{1.1}Ni_{0.48}Zr_{0.02})O_{16}$, Sinclair et al. (1980) proposed that the Ba is displaced off the special position to increase the Ba–Ba distances within a tunnel, thereby reducing intercation repulsions. Post et al. (1982) suggested, however, that the displacements of the tunnel cations result because the smaller of these cations ought to prefer positions closer to the nearest coordinating oxygen atoms, and thus the magnitude of the displacements ought to be a function of the size of the tunnel cation. In priderite (A cations: K > Ba), for example, they assumed that the subsidiary site was occupied by Ba and that the larger K was at the special position. Similarly, in cryptomelane and hollandite, the smaller tunnel cations (Sr^{2+} and Pb^{2+}) were assigned to satellite sites, displaced off the special position, but the larger cations (K^+ and Ba^{2+}) were assigned to the special position. Recent structure refinements of $K_{1.54}Ti_{7.23}Mg_{0.77}O_{16}$ (Weber and Schulz, 1983) and $BaTi_6V_2O_8$ (Szymański, 1986), however, show subsidiary sites and positional disorder even though there is only one kind of tunnel cation in each structure. Apparently there is more to the story than simply different tunnel positions being occupied by different kinds of tunnel cations. Both Post et al. (1982) and Sinclair et al. (1980) also suggested that the position of any given tunnel cation is affected by the contents of the tunnel in adjacent unit cells—whether vacancies or +1 or +2 cations—accounting further for some of the positional disorder. Recently, Weber and Schultz (1983) argued that the smeared-out electron density on the tunnel sites is evidence for diffusion of cations along the tunnels.

Although all of the above mechanisms are probably responsible to some degree for positional disorder of the tunnel cations, no mention has been made of the role lower-valence octahedral cations might contribute to the disorder. Recent studies using structure-energy calculations have revealed that the minimum-energy positions for the A cations in amphiboles (Docka et al., unpub. ms.) and Na^+ in high albite (Post and Burnham, 1984) are functions of the distributions and charges of framework cations. Thus, in these structures, many different local framework-cation configurations lead to varying local positions for the A-site cation in some amphiboles and for the Na^+ in high albite and, hence, cause the observed positional disorder. The hollandite structure is analogous to these two cases because it has cations in large cavities (the tunnel or A cations) surrounded by an octahedral framework occupied by a disordered arrangement of +4 and lower-valence cations (no structure refinements have detected any evidence of ordering on the octahedral sites). We have, therefore, used structure-energy calculations to investigate whether the minimum-energy tunnel-cation positions in various hollandite structures are functions of the arrangements of lower-valence octahedral cations and whether multiple configurations are likely to occur in a single crystal, thereby giving rise to the observed positional disorder.

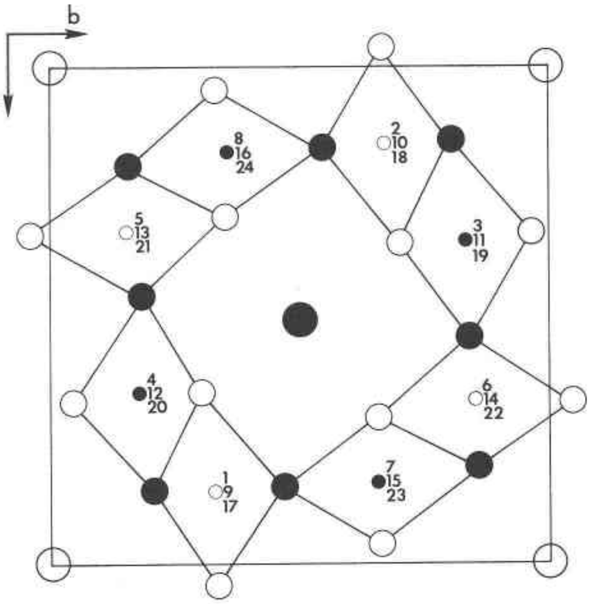

Fig. 1. Projection of *I*4/*m* hollandite structure down **c**. Small circles represent the octahedral (B) cations; medium-sized circles, the oxygen atoms; and large circles, the tunnel (A) cations. Open circles indicate atoms at $z = 0$, and solid circles, atoms at $z = 0.5$. Reference numbers 1–8 on the octahedral cations correspond to the first unit-cell along **c** ($z = 0$ to 1), 9–16 to the second cell, and 17–24 to the third cell.

CALCULATIONS

Structure-energy calcuations were performed using the computer program WMIN (Busing, 1981), modified to employ a Born exponential (Kittel, 1971) to calculate the short-range energy terms for anion-anion and anion-cation pair interactions (cation-cation repulsion terms were assumed to be negligible). The parameters in the Born exponential were derived for each ion pair (Table 1) from the MEG theory (Muhlhausen and Gordon, 1981) as described by Post and Burnham (1986). A shell-stabilized Hartree-Fock wave function with shell charge of +2 and radius of 1.01 Å was used for O^{2-} in the MEG calculations; 1.01 Å is the average of the shell radii calculated for O

Table 1. Born-type short-range energy parameters used in structure-energy calculations*

Ion pair	λ (kJ/mol)	ρ (Å)
Na–O**	563 165	0.2387
Mg–O	359 200	0.2457
Al–O	332 420	0.2461
K–O	6 297 550	0.2134
Ti–O	510 030	0.2523
Sr–O	1 670 545	0.2400
Ba–O	2 853 490	0.2401
O–O	291 000	0.2876

* From Post and Burnham (1986).
** O shell radius = 1.01 Å.

atoms in hollandite. The charged shell approximates the potential surrounding the O^{2-} within the crystal and serves to stabilize the anion. The Coulomb portion of the structure energy is summed by WMIN using the methods of Ewald (1921) and Bertaut (1952) to limits of 5.1 Å and 0.52 $Å^{-1}$ in direct and reciprocal space, respectively. All of the structure energies reported here include self-energy terms for O^{2-} (shell stabilized) → $O^{-1} + e^-$ of 1113 kJ/O atom.

The current MEG theory only allows consideration of closed-shell ions; therefore, in our calculations we used hollandite structures with Ti^{4+} and Al^{3+} or Mg^{2+} as octahedral cations, as occur in priderite, redlegite, and several synthetic hollandite compounds such as those investigated by Sinclair et al. (1980) and Beyeler (1976). We used the unit-cell parameters and coordinates for the framework atoms determined by Sinclair et al. (1980) for the tetragonal (*I*4/*m*) compound $(Ba_{0.98}Ca_{0.03})(Ti_{6.4}Al_{1.1}Ni_{0.48}Zr_{0.02})O_{16}$.

Energy minimizations for the case of half-filled tunnel sites were performed using the Rosenbrock search method, which does not use derivatives; although it is slower to converge than other techniques, it avoids saddle points and false minima (Busing, 1981). For calculations using a tripled cell with tunnel sites two-thirds filled, this method becomes extremely slow; we therefore switched to Newton's method (Busing, 1981), which does calculate derivatives, and we checked our results carefully for convergence. During the minimizations, we held the cell parameters and framework-atom positions fixed, allowing only the positions of the tunnel cations to vary. X-ray refinements of several hollandite structures with a variety of compositions show only slight differences in the framework-atom positions; furthermore, since the thermal parameters of the framework atoms are within expected ranges, there are no indications that these atoms are positionally disordered. Therefore, the assumption of an invariant framework is reasonable and should not significantly bias the results of our calculations. We determined minimum-energy tunnel-cation positions for a large number of configurations of lower-valence cations (Al^{3+} and Mg^{2+}) in the octahedral sites, using a variety of tunnel cations with total tunnel-site occupancies of one-half and two-thirds.

RESULTS OF CALCULATIONS

Half-filled tunnel sites

X-ray and electron-diffraction studies of hollandite minerals with half-filled tunnel sites (e.g., redlegite, hollandite, and coronadite) commonly reveal diffuse streaks halfway between the reciprocal lattice layers in the tunnel direction; such streaks indicate an ordering of the A cations on every other site along a given tunnel, but little ordering between tunnels (Post et al., 1982; Turner, 1982). The resulting superstructure has a *c* axis (parallel to the tunnels) double that of the simple unit cell. A recent refinement of the hollandite phase $BaTi_6V_2O_{16}$ in space group $I4_1/a$ revealed not only ordering of the Ba in alternate sites along a given tunnel but also three-dimensional ordering between tunnels (Szymański, 1986).

For model calculations on the half-filled hollandite phase $BaTi_6Al_2O_{16}$, we used a supercell with a double *c* axis and placed Ba^{2+} in every other special position along each tunnel. The resulting cell contains two occupied and two vacant tunnel-cation sites and 16 octahedral-cation sites. Four of the octahedral sites were filled with Al^{3+} to offset the charge on the two Ba^{2+} tunnel cations, and the remainder contained Ti^{4+}. The initial placements of the Ba^{2+} cations in specific tunnel sites is arbitrary because during the minimizations they are free to move. There are 1820 different ways to arrange the four Al^{3+} and 12 Ti^{4+} cations on the 16 octahedral sites. Because of the *I*4/*m* symmetry of the framework, however, we needed to consider only approximately 160 configurations. For all of these unique configurations, we performed energy-minimization calculations, allowing the positional parameters of both Ba^{2+} cations to vary simultaneously. A slightly different minimum-energy Ba^{2+} position results if only one of the Ba^{2+} cations per cell is allowed to vary, indicating that there is a small but significant interaction among Ba^{2+} cations in neighboring tunnels. The fact that this interaction is slight is consistent with the observation that few hollandite structures show three-dimensional ordering of tunnel cations.

The results of our calculations show that the minimum-energy Ba^{2+} positions are indeed a function of the arrangement of the Al^{3+} and Ti^{4+} cations on the octahedral sites. In Figure 2 we plot the calculated Ba^{2+} positions (two per cell) for each of the approximately 160 (Al^{3+},Ti^{4+}) configurations. Since special position 2a has 4/*m* symmetry, Figure 2 represents only one unique octant of the total distribution of Ba^{2+} positions. In nearly all of the cases modeled, the minimum-energy Ba^{2+} sites are displaced from the special position.

Figure 3 plots a histogram of structure energies after minimization of the Ba^{2+} positions for the (Al^{3+},Ti^{4+}) configurations represented in Figure 2. All of the energies plot between −5129 and −5163 kJ/O atom, and about two-thirds are bunched between −5148 and −5163 kJ/O atom. The most energetically favorable case [−5163 kJ/O atom] has Al^{3+} on octahedral sites 1, 2, 5, and 6 (Fig. 1), and the minimum-energy Ba^{2+} positions for this ar-

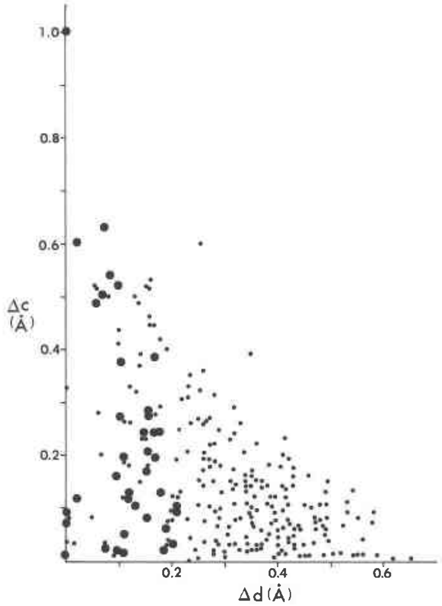

Fig. 2. Displacements from the special position (0,0,0), parallel (Δ*c*) and perpendicular (Δ*d*) to the tunnel direction, of the 300 calculated minimum-energy Ba^{2+} positions determined for 157 arrangements of 12 Ti^{4+} and 4 Al^{3+} cations on the 16 octahedral sites in a double hollandite cell with half-filled tunnel sites ($Ba_2Ti_{12}Al_4O_{32}$). Larger circles represent cases with no Al^{3+} cations in octahedra that share a common edge.

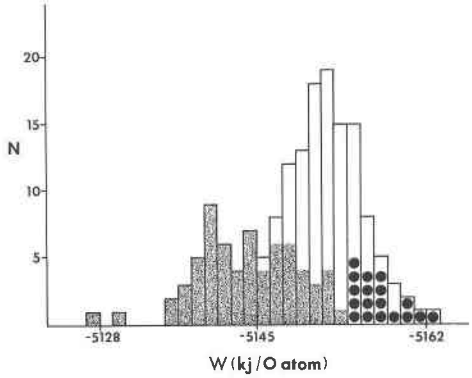

Fig. 3. Histogram showing calculated structure energies for half-filled hollandite ($Ba_2Ti_{12}Al_4O_{32}$) after minimizing the Ba^{2+} positions. The 157 distinct (Ti,Al) distributions correspond to those included in Figure 2. The shaded cases have (Ti,Al) configurations that place Al^{3+} cations in octahedra that share common edges within an octahedral chain (‖**c**). (Ti,Al) arrangements indicated by circles have no Al^{3+} cations in octahedra that share common edges.

rangement are at (0,0,0.16) and (0,0,0.504) [the special positions are at (0,0,0) and (0,0,0.5), respectively]. The calculated Ba^{2+} position at (0,0,0.16) is displaced 1.0 Å along the tunnel from the special position and does not correspond with tunnel-cation positions determined by X-ray refinement, suggesting that the octahedral cations in hollandite crystals are not ordered in the most energetically favorable way. The relatively narrow range of structure energies indicates that many and perhaps all of the possible (Al^{3+},Ti^{4+}) configurations occur in a given crystal of hollandite, leading to both short- and long-range disorder. Recall that both X-ray and neutron-diffraction experiments show long-range disorder on the octahedral sites, and neither X-ray nor electron-diffraction studies have found evidence of short-range order.

For the many octahedral-cation configurations that might exist in different unit cells in a hollandite crystal, our calculations show that the Ba^{2+} tunnel cations will occupy a variety of different positions. This situation will cause a smearing out of the electron density about the special position in the average unit cell determined by X-ray or neutron-diffraction structure refinements, and therefore will likely give rise to the observed subsidiary sites and large apparent thermal motion of the tunnel cations.

A closer look at Figure 3 shows that the structure energies approximate a bimodal distribution, with one peak centered at about −5141 and another at −5152 kJ/O atom. Comparision of octahedral-cation configurations and their corresponding structure energies reveals that in general the most energetically favorable cases have the Al^{3+} in octahedra that do not share a common edge (Fig. 3). Conversely, the least-favored arrangements, i.e., those forming the peak centered at −5141 kJ/O atom in Figure 3, have Al^{3+} cations in adjacent octahedra in the same octahedral chain with an Al–Al distance of 2.94 Å. The models yielding structure energies composing the bulk of the peak centered at −5152 kJ/O atom in Figure 3 typically have Al^{3+} in octahedra that share a common edge between octahedral chains with an Al–Al distance of 3.00 Å. This correlation between structure energy and degree of edge-sharing between Al octahedra is analogous to the aluminum avoidance rule (Loewenstein, 1954) observed for silicate minerals. It is likely that the unfavorable arrangements represented by the higher-energy peak in Figure 3 rarely, if ever, occur in hollandite structures and that the predominant configurations are those that have no edge-sharing Al octahedra, or perhaps minimal edge-sharing between octahedral chains.

Our calculated displacements along the tunnel (Δ*c*) of the Ba^{2+} cations from the special position range from 0 to 1.0 Å with mean displacement ≈ 0.11 Å. Approximately 90% of the minimum-energy Ba^{2+} positions have Δ*c* values between 0 and 0.35 Å. Although all of the X-ray refinements of hollandite structures have restricted the tunnel cations to the fourfold axis (twofold axis in *I*2/*m* structures), most of our calculated Ba^{2+} positions fall off the rotation axis. The displacements perpendicular to the tunnel direction (Δ*d*) range from 0 to 0.65 Å and typically are greatest for points in Figure 2 with small Δ*c* values. The rms Δ*d* for calculated Ba^{2+} positions with $\Delta c < 0.25$ Å is 0.34 Å and decreases to 0.18 Å for positions with Δ*c* from 0.25 to 0.55 Å and to 0.15 Å for $\Delta c > 0.55$ Å. In general, the Ba^{2+} positions with the larger Δ*d* values correspond to the energetically less favorable (Ti^{4+},Al^{3+}) con-

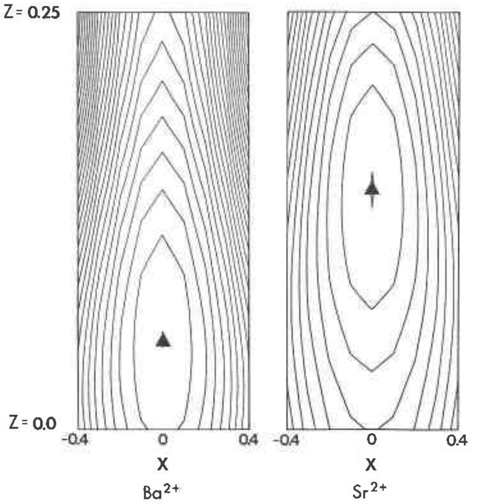

Fig. 4. Maps of structure energy versus tunnel-cation position for $Ba_2Ti_{12}Al_4O_{32}$ and $Sr_2Ti_{12}Al_4O_{32}$ with Al in octahedral sites 1, 2, 3, and 4 (see Fig. 1). Triangles mark the calculated minimum-energy positions. The plane of each map is an **x**-**z** section at **y** = 0; the special position (0,0,0) lies in the plane. Contour interval is 0.25 kJ/O atom. All framework atoms lie in planes parallel to (001) at $z = 0$ and $z = 0.25$ of the doubled cell.

figurations, e.g., those in the peak centered at −5141 kJ/O atom in Figure 3. If only cases that have no edge-shared Al octahedra are considered, then the greatest calculated $\Delta d \approx 0.2$ Å (see Fig. 2). The fact that refined temperature factors perpendicular to the tunnels at the special position are typically in the range of $u = 0.015$–0.03—corresponding to rms displacements from 0.12 to 0.17 Å—further supports the conclusion that octahedral-cation arrangements containing lower-valence cations in octahedra that share common edges probably do not occur frequently in hollandite crystals.

The calculated Ba^{2+} distribution (Fig. 2) for the most part compares very well with results from X-ray studies of hollandite structures having half-filled tunnel sites, particularly if only the cases in Figure 2 without edge-sharing Al octahedra are considered. Most structure refinements have split the tunnel cations into two locations, a main site on the special position and a lesser occupied subsidiary site displaced some distance along the tunnel, both with relatively large temperature factors. This is consistent with our model distribution in Figure 2 which shows most of the Ba^{2+} positions clustered around the special position, but with a range of Δd and Δc values that would give rise to a large apparent temperature factor, and a second smaller cluster of points centered at $\Delta c = 0.50$ Å. In his structure refinement of $BaTi_6V_2O_{16}$, Szymański (1986) obtained site-occupancy factors of 0.80 for Ba^{2+} at the special position and 0.06 at a subsidiary site displaced 0.45 Å along the tunnel; these compare well with our model predictions. The refined temperature factors indicate a rms displacement of 0.17 Å parallel to the tunnel for the site at the special position, which is close to the value of 0.15 Å calculated for the cluster of Ba^{2+} positions near the special position in Figure 2.

The tunnel-cation distribution refined by Post et al. (1982) for the mineral hollandite $[(Ba_{0.75}Pb_{0.16}Na_{0.10}K_{0.04})(Mn^{4+},Mn^{3+},Fe^{3+},Al^{3+})_8O_{16}\cdot H_2O]$ also is similar to our calculated results, although the presence of other types of tunnel cations in addition to the Ba^{2+} makes direct comparison of the observed and model structures more difficult. Post et al. (1982) observed two tunnel-cation sites, one at the special position and a subsidiary site displaced about 0.60 Å along the tunnel, with both sites having large temperature factors parallel to the tunnel direction. They assumed that the smaller Pb^{2+} cations would favor the displaced site, which is closer to the nearest-neighbor oxygen atoms, and assigned the Ba^{2+} to the special position. The results of our calculations on $BaTi_6Al_2O_{16}$ and the structure refinement for $BaTi_6V_2O_{16}$ indicate, however, that Ba^{2+} and Pb^{2+} are probably mixed over the two tunnel-cation positions. The refined occupancies for the two tunnel sites (assuming equal amounts of Pb^{2+} and Ba^{2+} at each site) are 0.70 at the special position and 0.30 at the satellite position, a result with which our model calculations are in reasonably good agreement. The greater apparent occupancy of the subsidiary site in the Pb-containing structure compared with $BaTi_6V_2O_8$ may occur because—as we discuss below—the smaller Pb^{2+} cations ought to be more displaced than the Ba^{2+} cations.

In order to explore the expected relative displacements of Ba^{2+} and Pb^{2+} in hollandite, we calculated structure-energy maps over the tunnel sites for Ba^{2+} and for Sr^{2+}, which has an ionic radius similar to that of Pb^{2+}, using the same (Ti^{4+},Al^{3+}) configuration in each case (Al^{3+} in sites 1, 2, 3, and 4, Fig. 1). For each calculation, the structure framework was held fixed, and the tunnel cation was moved to points on a grid covering the tunnel sites; structure energies were calculated at each gridpoint. The contoured maps in Figure 4 show that the minimum-energy position for the smaller Sr^{2+} is displaced 0.9 Å along the tunnel from the special position compared with a shift of only 0.3 Å for Ba^{2+}. Minimization calculations for Sr^{2+} and Ba^{2+} tunnel cations, using a variety of (Ti^{4+},Al^{3+}) configurations, show in general that the smaller cation is more displaced both parallel and perpendicular to the tunnel directions. Thus, the smaller Pb^{2+} in the mineral hollandite will be more displaced than the large Ba^{2+}, and it is therefore expected that the subsidiary site will have a greater occupancy factor than in structures where Ba^{2+} is the only tunnel cation. This is probably also the reason why the subsidiary site refined for hollandite is more displaced than the subsidiary site in $BaTi_6V_2O_{16}$ or our model (0.60 vs. 0.50 Å). The maps in Figure 4 also show that the minimum valley for Sr^{2+} is broader and shallower than for Ba^{2+}, suggesting that smaller cations will show larger temperature factors. In both of the structure-energy maps in Figure 4, the minimum valleys are widest closest to the special position, which is reasonable, since the effective cross section of the tunnel is also greatest for the plane containing the special position, and which is consistent with the distribution of Ba^{2+} positions in Figure 2.

Sinclair et al. (1980) refined the structure of the half-filled hollandite compound $(Ba_{0.98}\,Ca_{0.03})\,(Ti_{6.4}\,Al_{1.10}\,Ni_{0.48}Zr_{0.02})O_{16}$ and, rather than using a split tunnel-cation site, placed all the Ba^{2+} at a position displaced 0.33 Å along the tunnel from the special position. The large temperature factor for the Ba^{2+} ($U_{33} = 0.054$) and the relatively high *R* value of 5.9% combined with peaks near the tunnel-cation site in the final difference Fourier map of +4 and +2.2 $e^-/Å^3$ suggest that perhaps a model with split tunnel-cation sites might provide a better fit to the observed electron density in the tunnels. Furthermore, since the lower-valence octahedral cations are a mixture of +2 and +3 cations, the resultant distribution of Ba^{2+} positions will in all likelihood be different from that for +3 cations only. In general, though, their results are consistent with other studies of hollandites in that they show the existence of positional disorder in the tunnels, similar to what our calculations predict would arise from having a disordered arrangement of octahedral cations.

Two-thirds-filled tunnel sites

Many hollandite minerals and compounds, particularly those containing K^+ and Na^+ tunnel cations, have tunnel sites that are two-thirds to three-fourths occupied. As with half-filled hollandite structures, X-ray and electron-diffraction experiments in many cases reveal diffuse streaks between reciprocal lattice planes in the tunnel direction (Turner, 1982; Beyeler, 1976; Pring and Jefferson, 1983), indicating that ordering of the cations within individual tunnels commonly occurs every three or four unit cells for tunnel occupancies of two-thirds and three-fourths, respectively. For our model calculations, we assumed a hollandite structure with the tunnel sites two-thirds occupied, having the basic formula $K_{1.33}(Ti_{7.33}Mg_{0.67})O_{16}$. We constructed ordered supercells using atom positions reported by Sinclair et al. (1980) and tripled the length of the *c* axis. We filled four of the six possible tunnel sites with K^+ (two in each tunnel) and distributed 22 Ti^{4+} and two Mg^{2+} over the 24 octahedral-cation sites. We performed minimization calculations for the 11 unique (Ti^{4+},Mg^{2+}) arrangements, allowing the positions of all four K^+ cations to vary simultaneously.

The distribution of minimum-energy K^+ positions (four per calculation) is plotted in Figure 5. It resembles Figure 2 in that the majority of points cluster near the special position with a second smaller clustering of points shifted along the tunnel. In this case, however, the clusters are better resolved with the second cluster located 0.5–0.7 Å from the special position as opposed to 0.4–0.6 Å for the half-filled case; furthermore, a larger fraction (25%) of the positions fall within the displaced cluster. The Δc values for the K^+ positions represented in Figure 5 range from 0 to 0.7 Å, and again the displacements perpendicular to the fourfold axis are greatest for positions with small Δc values.

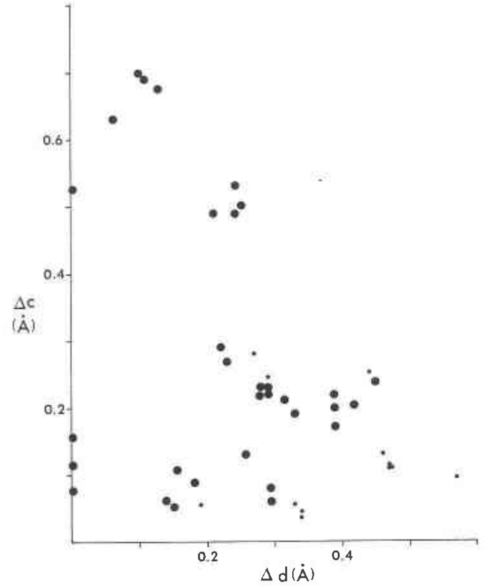

Fig. 5. Displacements from the special position (0,0,0), parallel (Δc) and perpendicular (Δd) to the tunnel direction, of the 44 calculated minimum-energy K^+ positions determined for the 11 unique arrangements of 22 Ti^{4+} and 2 Mg^{2+} cations on the 24 octahedral sites in a triple hollandite cell (along **c**) with two-thirds-filled tunnel sites ($K_4Ti_{22}Mg_2O_{48}$). Larger circles represent cases with no Mg^{2+} cations in octahedra that share a common edge.

The structure energies after minimization for the various (Ti^{4+},Mg^{2+}) configurations range from −5743 to −5759 kJ/O atom. The most energetically favorable case has Mg^{2+} in octahedral sites 1 and 3 (Fig. 1), yielding minimized K^+ positions at (0.50,0.52,0.20), (0.00,0.02, −0.03), (0.51,0.50,0.83), and (0.01,0.00,0.34) [special positions are at (0.5,0.5,0.167), (0,0,0), (0.5,0.5,0.833), and (0,0,0.33), respectively]. As with $BaTiAl_2O_{16}$, the relatively tight grouping of structure energies (8 of 11 are within 5.4 kJ/O atom of each other) suggests that the octahedral cations are probably disordered in crystals of hollandite compounds and minerals. Also, the energetically least favorable arrangements involve edge-sharing of Mg^{2+} octahedra.

Structure refinements have been reported for two hollandite minerals with tunnel sites that are approximately two-thirds occupied—cryptomelane [$(K_{0.94}Na_{0.25}Sr_{0.13}Ba_{0.1})_{1.42}(Mn^{4+},Mn^{3+},Fe^{3+},Al^{3+})_8O_{16}\cdot H_2O$] (Post et al., 1982) and priderite [$(K_{0.90}Ba_{0.35}Na_{0.06})_{1.31}(Ti^{4+},Fe^{3+},Mg^{2+})_8O_{16}$] (Post et al., 1982; Sinclair et al., 1982)—and for the compound $K_{1.54}(Ti_{7.23}Mg_{0.77})O_{16}$, which has tunnel sites that are about three-quarters filled. In all of these structures, the tunnel cations are split into a main site at the special position and a subsidiary site displaced 0.55 Å (cryptomelane and priderite) or 0.74 Å ($K_{1.54}Ti_{7.33}Mg_{0.77}O_{16}$) along the tunnel. In cryptomelane and priderite, approximately 20% and 30%, respectively, of the electron densities in the tunnels are at the subsidiary sites, values that compare well with our model distribution in Figure 5 showing about 25% of the K^+ positions in a cluster centered at about $\Delta c = 0.6$ Å. Refined temperature and occupancy factors were not reported for $K_{1.54}Ti_{7.23}Mg_{0.77}O_{16}$. Overall, the observed split tunnel-cation sites and their relative occupancies—combined with relatively large refined apparent temperature factors for all of the tunnel-cation sites, especially in the tunnel direction ($U_{11} = 0.013$–0.021; $U_{33} = 0.036$–0.076)—indicate an observed electron-density distribution that compares very well with that in Figure 5.

The structure refinements for cryptomelane and priderite (Post et al., 1982) reveal small electron-density peaks halfway between the special positions in the tunnels, which Post et al. (1982) assumed were due to Na^+. To examine this assumption we carried out a series of minimizations as above but with Na^+ instead of K^+ in the tunnels. Our results show that the smaller Na^+ is more displaced, relative to K^+, both parallel and perpendicular to the tunnels for a given (Ti^{4+},Mg^{2+}) configuration. In fact, about one-third of the minimized Na^+ positions cluster about a point that is approximately midway between the special positions. Thus, our calculations support the assumption that the extra electron-density peaks in the tunnels of cryptomelane and priderite are likely to be caused by Na^+.

SUMMARY

Our model calculations show that the minimum-energy positions for the tunnel cations in hollandites are related to the configuration of the lower-valence cations in the octahedral sites, and the narrow range of structure energies calculated for many of the configurations suggests that the octahedral cations are probably disordered in most hollandite structures. Therefore, a hollandite crystal will contain a large variety of arrangements of octahedral cations in different unit cells and correspondingly a range of tunnel-cation positions. X-ray and neutron-diffraction structure refinements reveal only an average unit cell containing a superposition of tunnel-cation positions that give rise to the observed split sites and positional disorder. Our calculations also show, however, that octahedral-cation arrangements resulting in lower-valence cations in octahedra that share common edges are energetically unfavorable and probably are not common in hollandite crystals. We have modeled tunnel-cation positions in hollandite structures having all possible unique octahedral-cation configurations for tunnel-site occupancies of one-half and two-thirds. In both cases the distribution of calculated minimum-energy tunnel-cation positions matches quite well with experimentally determined electron-density distributions for a variety of hollandite phases. Overall, the distributions of calculated minimum-energy tunnel-cation positions for the two cases are quite similar. Both show a majority of the calculated positions clustered about the special position and a smaller cluster of positions displaced along the tunnel from the special position. In the distribution for the two-thirds-filled hollandite, however, the two groupings are better resolved, and there is a greater fraction of positions in the cluster that is shifted away from the special position.

Our model calculations show that, in general, smaller tunnel cations will be more displaced from the special position than larger cations. Also there is a slight but significant interaction among tunnel cations in neighboring tunnels, particularly in the case of Ba^{2+} (and other divalent cations).

Although the results of our calculations provide a basic understanding of the positional disorder exhibited by tunnel cations in hollandite structures, we have not considered complexities inherent in many hollandite compounds and minerals, such as presence of water in tunnels, monoclinic instead of tetragonal symmetry, and incommensurate ordering of tunnel cations (Bursill and Grzinic, 1980). Certainly these variations will affect the details of the tunnel-cation distribution in a given structure, but probably not enough to change our overall conclusions.

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REFERENCES

Abbott, R.N., Jr. (1984) Al-Si ordering in 1M micas? Geological Society of America Abstracts with Programs, 16, 424.

Bertaut, Felix. (1952) L'énergie électrostatique de Reseaux ioniques. Le Journal de Physique et le Radium, 13, 499–505.

Beyeler, H.U. (1976) Cationic short-range order in the hollandite $K_{1.54}Mg_{0.77}Ti_{7.23}O_{16}$: Evidence for the importance of ion-ion interactions in superionic conductors. Physical Review Letters, 37, 1557–1560.

Brown, G.E., and Fenn, P.M. (1979) Structure energies of the alkali feldspars. Physics and Chemistry of Minerals, 4, 83–100.

Bursill, L.A., and Grzinic, G. (1980) Incommensurate superlattice ordering in hollandites $Ba_xTi_{8-x}Mg_xO_{16}$ and $Ba_xTi_{8-2x}Ga_{2x}O_{16}$. Acta Crystallographica, B36, 2902–2913.

Busing, W.R. (1981) WMIN, a computer program to model molecules and crystals in terms of potential energy functions. U.S. National Technical Information Service, ORNL-5747.

Cadee, M.C., and Verschoor, G.C. (1978) Barium tin chromium oxide, a new hollandite phase. Acta Crystallographica, B34, 3554–3558.

Chamberlain, C.P., Docka, J.A., Post, J.E., and Burnham, C.W. (1985) Scapolite: Alkali atom configurations, antiphase domains, and compositional variations. American Mineralogist, 70, 134–140.

Cohen, R.E., and Burnham, C.W. (1985) Energetics of ordering in aluminous pyroxenes. American Mineralogist, 70, 559-567.

Ewald, P.P. (1921) The calculation of optical and electrostatic lattice potentials. Annals of Physics (Leipzig), 64, 253–287.

Giese, R.F., Jr. (1975) Electrostatic energy of columbite/ixiolite. Nature, 256, 31–32.

Kittel, Charles. (1971) Introduction to solid state physics, 4th edition. Wiley, New York.

Loewenstein, Walter. (1954) The distribution of aluminum in the tetrahedra of silicates and aluminates. American Mineralogist, 39, 92–96.

Muhlhausen, C., and Gordon, R.J. (1981) Electron-gas theory of ionic crystals, including many-body effects. Physical Review, B23, 900–923.

Post, J.E., and Burnham, C.W. (1984) Disordering in high albite: Insights from electrostatic energy minimizations. Geological Society of America Abstracts with Programs, 16, 625.

——— (1986) Ionic modeling of mineral structures and energies in the electron gas approximation: TiO_2 polymorphs, quartz, forsterite, diopside. American Mineralogist, 71, 142–150.

Post, J.E., Von Dreele, R.B., and Buseck, P.R. (1982) Symmetry and cation displacements in hollandites: Structure refinements of hollandite, cryptomelane, and priderite. Acta Crystallographica, B38, 1056–1065.

Pring, A., and Jefferson, D.A. (1983) Incommensurate superlattice ordering in priderite. Mineralogical Magazine, 47, 65–68.

Sinclair, W., and McLaughlin, G.M. (1982) Structure refinement of priderite. Acta Crystallographica, B38, 245–246.

Sinclair, W., McLaughlin, G.M., and Ringwood, A.E. (1980) The structure and chemistry of a barium titanate hollandite-type phase. Acta Crystallographica, B36, 2913–2918.

Szymański, Jan T. (1986) The crystal structure of mannardite, a new hydrated cryptomelane-group (hollandite) mineral with a doubled short axis. Canadian Mineralogist, 24, 67–78.

Turner, Shirley. (1982) A structural study of tunnel manganese oxides by high-resolution transmission electron microscopy. Ph.D. Dissertation, Arizona State University, Tempe.

Weber, Hans-Peter, and Schulz, Heinz. (1983) Atomic disorder and thermal behaviour of a synthetic potassium hollandite. Geological Society of America Abstracts with Programs, 15, 715.

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