MINERALOGICAL NOTES

A COMPARISON OF OH⁻ MOTIONS IN BRUCITE AND MICAS[1]

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Despite analogous atomic arrangements of Mg and OH, brucite $(Mg(OH)_2)$ and phlogopite $(KMg_3(OH)_2(AlSi_3)O_{10})$ present striking differences in their infrared spectra. A single absorption band due to OH stretching is observed in phlogopite whereas brucite has a total of 15 bands on both sides of the fundamental. A comparison of the two structures (Figs. 1, 2) suggests that the complex spectrum for brucite results from interactions among neighboring hydroxyl ions, not present in phlogopite.

The intensity of the OH stretching band at 3700 cm⁻¹ is highly sensitive to the orientation of the single crystal and varies in such a way as to indicate that hydroxyl ions are perpendicular to the (001) plane (Bassett, 1960, Serratosa and Bradley, 1958). The spectrum of brucite also shows an absorption band at 3700 cm⁻¹, which is sensitive to orientation, but in addition it shows 15 other absorption bands distributed above and below 3700 cm⁻¹ (Mara and Sutherland, 1953). Only two of these are somewhat sensitive to orientation, the others are relatively insensitive. It is interesting to note that the infrared spectrum for muscovite has a single absorption band at 3600 cm⁻¹ which is also relatively insensitive to crystal orientation (Bassett, 1960; Serratosa and Bradley, 1958; Tsuboi, 1950). This absorption band has been attributed to hydroxyl ions whose dipoles are inclined to the (001) plane because they are bound to 2 Al ions which are asymmetrically arranged below the OH⁻ ions instead of three Mg ions symmetrically arranged as in phlogopite. The lower frequency of absorption of the hydroxyl ion in the muscovite spectrum has been attributed to a lower force constant for this ion resulting from the higher charge of the aluminum ions (Bassett, 1960).

The multiplicity of absorption bands in alkali and alkaline earth hydroxides has received considerable attention, and two interpretations have recently been proposed: (1) Hexter and Dows, 1956; Hexter, 1958, 1960. (2) Wickersheim, 1959; Buchanan *et al.* 1962.

Hexter reports symmetry of the side bands with respect to the fundamental stretching vibration of the OH⁻ and concludes from this that the side bands can be explained by combinations of the fundamental stretching vibration with librational motion of the hydroxyl ions "without

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knowledge of each other's presence." Wickersheim (1959) and Buchanan *et al.* (1962) do not observe symmetry of the positions of the side bands and attribute them to combinations of "lattice" vibrational modes with OH⁻ stretching vibrations. They also find evidence, from experiments with deuterated samples, of interactions among hydroxyl ions.

Safford, Brajovic and Boutin (to be published) have recently investigated the low energy vibrational levels in polycrystalline samples in $Mg(OH)_2$ and $Ca(OH)_2$ by inelastic scattering of slow neutrons and conclude from their data that Hexter's model is questionable because they find evidence that there must indeed be interactions among OH⁻ ions. However, their spectra are not in disagreement with the model of Buchanan *et al.* (1962) (combined "lattice" vibrations and OH⁻ stretching vibrations).

We believe that a comparison of the hydroxides with the micas can shed light on the complex mechanisms involved in the hydroxide spectra. In the first of the two models mentioned above stretching vibrations combine with libration of the OH⁻ ions. It is not immediately clear why such a mechanism should not be operative in the phlogopite structure as well, especially if the OH⁻ ions do not influence each other as suggested by
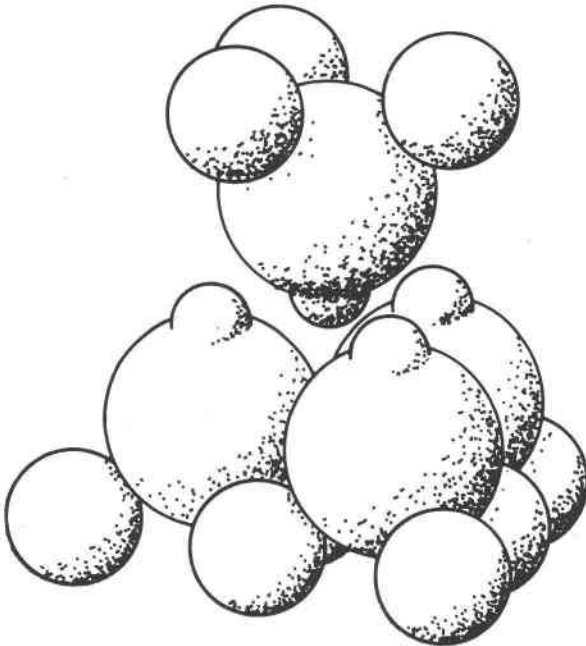

Fig. 1. Brucite structure. Small spheres are Mg, large spheres are O and bumps are H. Note close proximity of OH ions.
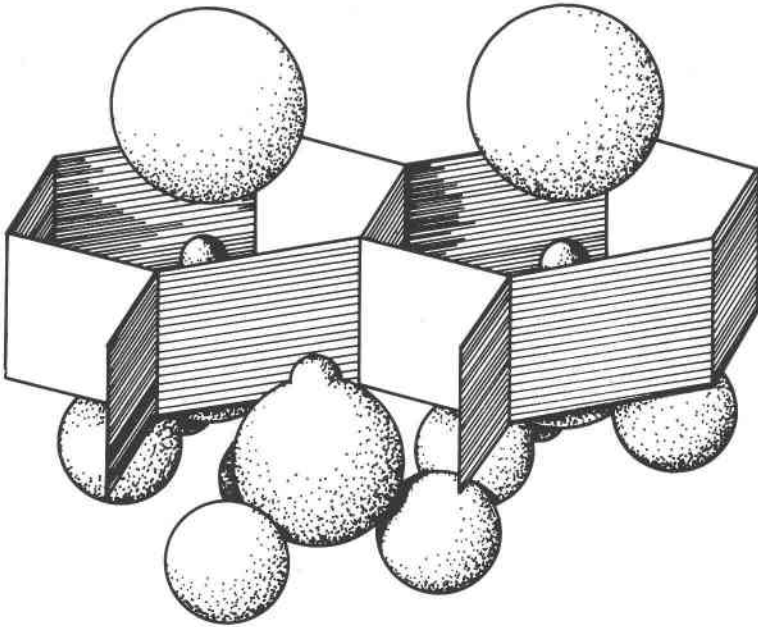
Fig. 2. Phlogopite structure. Small spheres are Mg, medium sized spheres are O, bumps are H, large spheres are K and "honeycomb" represents silica and alumina tetrahedral sheet. Note that the OH ions are isolated in cells of the tetrahedral sheet.

Hexter. Yet, only the fundamental stretching frequency of 3700 cm^{-1} is observed in the phlogopite spectrum.

Similarly, the "lattice" modes diagrammed by Buchanan *et al.* (1962) for LiOH should be operative in the phlogopite structure as well.

We believe that the mechanism most important in producing the multiplicity of bands in the brucite spectrum is the close proximity of hydroxyl ions causing these ions to have various orientations and force constants. Some biotites show two absorption frequencies in the 3600–3700 cm^{-1} region. Absorption at the higher frequency is sensitive to crystal orientation, but absorption at the lower frequency is not (Bassett, 1960). This pattern results from the presence of both Fe^{2+} and Fe^{3+} in the octahedral layer of the biotite corresponding to Mg^{2+} and Al^{3+}, respectively in phlogopite and muscovite. Thus, in the spectra of biotite micas we find a multiplicity of absorption bands due to different orientations and different force constants of the hydroxyl ions resulting from differences in the ionic environment.

As it seems impossible to explain the infrared spectrum of brucite by only a single stretching vibration perpendicular to the (001) plane or by a

combination of the stretching vibration with librational motion of the hydroxyl ions, it is suggested that there may be several possible orientations of the hydroxyl ion with respect to the (001) plane just as there are two of them in biotite. Each hydroxyl ion may form a weak transient "hydroxyl bond" with each of the three nearest hydroxyl ions in the layer above, but over a period of time the hydroxyl ion orientations are symmetrical about the c-axis. The sharp and intense peak at 47 mev observed in the neutron inelastic spectrum suggests a cooperative process. When any hydroxyl is inclined to the (001) plane, it forces the next hydroxyl to reorient itself in turn and the process is so generated throughout the entire crystal. The orientation perpendicular to the (001) plane is still, however, the most probable one, but the force constant of each hydroxyl ion and, therefore, its frequency of vibration is dependent upon the different bonding energies met by the hydroxyl ion in its different orientations. The multiplicity of absorption bands may result from various combinations of these vibrational frequencies.

Neutron diffraction data were also taken on a single crystal of brucite to try to find evidence for several orientations of the hydroxyl ions. A difference projection along the c-axis was obtained by synthesizing $[F_{obs.} - F_{calc.}(Mg,O)]$ for each reflection in reciprocal space: The position of the magnesium and oxygen atoms being well known from x-ray data, it is possible to calculate their contributions to the structure factors and this may be subtracted from the observed structure factors to give the contribution of the hydrogen only. The hydrogen atoms are not symmetrically distributed around the oxygen position as would be expected in that projection if the proton were located directly above the oxygen and vibrating along the c-direction. Instead the hydrogen peaks are smeared in different directions much more than could be accounted for by asymmetric effects of thermal motions. The peaks corresponding to Mg and O are well defined and this is a reasonably good test of monocrystallinity. This uncertainty might be attributed to the small number of reflections (12) observed in that projection. However, Busing and Levy (1957) in a similar neutron diffraction study of the isostructural $Ca(OH)^2$ along the b-axis, with more observed reflections (53), suggested that a model with a simple vibration along the c-axis (as proposed by Bernal and Megaw, 1935) may not be adequate to describe the structure. An attempt was also made by Petsch (1957, 1961) to plot a difference map from x-ray data of calcium hydroxide. However, because of the very small structure factor differences involved in his synthesis, this map should not be used to draw definite conclusions about the hydrogen positions.

In conclusion, a comparison of infrared spectra of brucite and micas indicates that there might be several possible orientations for the hy-

droxyl ions in brucite. Weak bonds may then exist between neighboring hydroxyl ions, giving rise to a cooperative process orienting the dipoles. Neutron inelastic scattering and neutron diffraction studies have provided confirming evidence.

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MANGANBERZELIITE FROM FRANKLIN, NEW JERSEY[1]

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Manganberzeliite has been identified in a few specimens from Franklin, New Jersey, as granular veinlets up to $\frac{3}{4}$ inch thick cutting franklinite-willemite ore. No other minerals are associated in the veinlets. A chemical

[1] Mineralogical Contribution No. 409, Harvard University.