

### ADDITIVITY IN THE PHYSICAL AND THERMODYNAMIC PARAMETERS OF OXIDES AND SILICATES

The molecular volume or density of a compound oxide may be determined approximately by summing the volumes of the corresponding simple oxides. This applies also to  $K$ ,  $l$ ,  $b$ ,  $d_1$ , and the thermodynamic parameters. The summation is by volume and in proportion to the volume, not by the number of simple oxides in the formula or by the molecular weights of these.

Table 2 gives the actual values (experimental or calculated, bottom line) as well as those found by additivity (top line). Not all parameters have been determined for certain substances (dash in the bottom line). The oxides give good agreement between the two figures when the cation in the simple oxide has the same coordination as in the compound. For instance,  $Mg^{2+}$  in periclase has  $k = 6$ , whereas in spinel it has  $k = 4$ , so we do not obtain very good agreement for spinel on summing over the volumes of periclase and corundum, but the ratio of the corresponding quantities usually corresponds to the  $MgO/Al_2O_3$  volume ratio. Another case occurs in zinc spinel and chrysoberyl, where the coordination is retained and the agreement is better.

The silicates give a more complicated picture. Low values for the densities are obtained on summing the volumes of the corresponding metal oxides and quartz: this suggests that the silicon-oxygen tetrahedra in silicates (which involve oxygen close packing) are packed more closely than in quartz. This agrees well with the known structure of quartz, which in Belov's representation [1] is derived from a cell with an  $A_3X_2$  pattern of eight cube-octahedra by filling two tetrahedra in each cube-octahedron along a three-fold axis. The energy relationships of the cations and anions cause the silicon-oxygen tetrahedra to rotate somewhat into a more stable position; the diad axes of those tetrahedra in quartz are parallel to the triad axis in the structure. The result is fairly open framework of tetrahedra that does not correspond to closest packing of the oxygen ions (about 1/3 of the close-packed positions are empty). Coesite has a denser structure, in which those diad axes are turned somewhat one with respect to another [2]. Belov's scheme [1] allows one to imagine also a closer packing of the tetrahedra.

The additivity method can give the parameters of forsterite, fayalite, enstatite, ferrosilite, phenakite, etc. with fair accuracy if we use  $SiO_2$  in the form of coesite (molecular volume  $20 \text{ cm}^3/\text{mole}$ , density  $3.0 \text{ g/cm}^3$ ) as the basis.  $K$  has not yet been determined for coesite, which causes difficulty in calculating  $K$  for silicates. The dependence of  $K$  on the mean atomic volume [23] and a reverse calculation by additivity give  $K = 8 \times 10^5 \text{ kg/cm}^2$  as an approximate result, which was used in calculating the other  $K$ .

However, certain minerals (e.g., kyanite and garnet) have the tetrahedra more closely packed than in coesite; they correspond to a modification of  $SiO_2$  having the parameters  $M/\rho = 18.5 \text{ cm}^3/\text{mole}$ ,  $\rho = 3.25 \text{ g/cm}^3$ , and  $K = 11 \times 10^5 \text{ kg/cm}^2$ . Such a modification is not known, but the features of quartz and coesite enable us to assume that it could occur, at least in the metastable state. This allows us to calculate the properties of kyanite, garnets, and the spinel modifications of forsterite and fayalite having densities of  $3.53$  and  $4.85 \text{ g/cm}^3$  respectively (spinel I in Table 1).

$K$  has not been determined for kyanite; the calculation gives about  $19 \times 10^5 \text{ kg/cm}^2$ . To test this I derived approximately the longitudinal wave speeds  $V_p$  along the [001], [010], and [100] directions in a kyanite crystal as  $10.8$ ,  $10.2$ , and  $8.0 \text{ km/sec}$  respectively. For transverse waves,  $V_s$  was  $6.3$ ,  $5.3$ , and  $4.5 \text{ km/sec}$  for different directions of displacement.  $K$  was calculated via the mean values  $V_p = 9.70 \text{ km/sec}$  and  $V_s = 5.70 \text{ km/sec}$  ( $V_p/V_s = 1.73$ , as for corundum), which gave  $K$  as  $18.7 \times 10^5 \text{ kg/cm}^2$ . Higher  $K$  are implied by  $K = f(\bar{v})$  [23].

It is difficult to calculate the parameters of sillimanite and andalusite in this way because some of the  $Al^{3+}$  ions have  $k = 4$ , and the physical properties of these tetrahedra are unknown. The situation is similar for the feldspars. The divalent cations in garnets have  $k = 8$  (at centers of Thomson cubes) [1] and their properties are unknown. Somewhat high values for the volumes are obtained if we use as a basis the properties in 6:6 coordination in conjunction with  $18.5 \text{ cm}^3/\text{mole}$  for silica.

The additivity principle may be used to find approximate densities, volumes, etc. for high-pressure phases, e.g., the spinel II modification of forsterite or enstatite (Table 1),