A SURVEY OF CHEMICAL BONDING IN SILICATE MINERALS BY X-RAY EMISSION SPECTROSCOPY[1,2]

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ABSTRACT

A survey has been made of the Kβ-band X-ray spectra of crystalline silicates having particular significance as rock-forming minerals. These include representative orthosilicates, pyrosilicates, and framework and chain silicates. Aluminum Kβ-band spectra of tetrahedrally coordinated Al proxying for Si, in both ordered and disordered structures, were found to be similar to the Si Kβ-band specta of the same minerals. The Si-O bond strengths were found to vary as a function of the apparent degree of orbital overlap, as determined by known Si-O-M bond angles, where M is another cation. Decrements in Si-O bond strengths relative to SiO_2 were measured in terms of electron volts or kilocalories per mole.

INTRODUCTION

Many of the unsolved structural problems of mineralogy and crystallography involve questions of the assignment of cations to alternate crystallographic sites, or the coordination numbers of specific cations with respect to oxygen, or the nature of the specific type of chemical bonding involved, or similar ambiguities that cannot be resolved with the aid of diffraction data alone. In attacking such problems it frequently has been helpful to utilize additional information that can be obtained by spectroscopic methods. Among the most useful supplemental tools are optical spectroscopy, Mossbauer spectroscopy, magnetic resonance spectroscopy, and X-ray spectroscopy. Of these, X-ray spectroscopy has probably attracted the least interest in recent years from mineralogists who have been frustrated by the limitations of X-ray crystallographic Fourier analysis. X-ray spectroscopy appears, however, to possess great potential because it is capable, in principle, of elucidating the electronic structure of a specific element in a compound and because the X-ray spectrum of an element is a function of its average immediate environment. Mossbauer spectroscopy possesses similar specificity, but it is applicable only to iron and a few other elements of less general interest.

In previous papers we have explored the application of molecular orbital (MO) theory concepts to the interpretation of spectral band

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splitting of both X-ray absorption (Glen, 1968) and X-ray emission spectra of crystalline (Dodd, 1968a) and amorphous solids (Dodd, 1968b). We have found that MO theory, together with band theory concepts and the use of models of known crystal structures, including orbital models, can be used to make assignments of observed peaks to specific electronic transitions. MO theory has been applied primarily to interpretations of molecular bonding, as in organic compounds. Insofar as it relates primarily to the short-range bonding of nearest neighbors, however, MO theory also is useful as a first approximation for interpreting chemical bonding in oxide solids, including rock-forming minerals. The wealth of X-ray crystallographic structural information concerning silicates may thus be drawn on for use in the interpretation of X-ray spectra, specifically the X-ray emission $K\beta$-band spectra of silicon and aluminum. In this manner one may observe indicated π-bonding in these oxides and relate the stability of Si-O and Al-O bonds in specific structures to similar bonds in SiO_2 and α-Al_2O_3, or other suitable reference structures. This paper represents a first approach to assess the strengths and weaknesses of these ideas.

Experimental

Experimental procedures employed have been described previously (Dodd, 1968a). X-ray emission spectra were measured by adapting electron microprobes for use as X-ray spectrometers. Samples were mounted, ground flat, and polished with 1-μm and 1/4-μm diamond grit, followed by application of a 200 Å film of carbon, as for electron microprobe microanalysis; but sample surfaces were relatively large, measuring 5 to 10 mm in diameter. Electron beams used for excitation were frequently defocussed to cross-sections as large as 200- to 300-μm in diameter; and the total sample current was increased to the extent required to produce appropriate X-ray peak intensities, suitable for ratemeter scanning of the spectra. The current densities of required electron beam sample currents were minimized by the defocussed beams. Occasionally the beam was scanned electronically over a line on the sample surface parallel to the axis of the Rowland circle (or the axis of rotation of the analyzing crystal). Sample overheating (a problem encountered in measuring Al $K\beta$-band spectra of samples containing moderate concentrations of aluminum, for example) was reduced further by mechanical translation of specimens under the electron beam at rates of 20- to about 200-μm/min. during measurement; hence the need for a large sample surface.

Standard procedures with respect to electron beam potential (20 keV) and choice of analyzing crystal (ADP) were adopted, following experience gained in the earlier work. (The increased dispersion of currently available PET crystals would be preferable.) Wavelength calibration also followed the previous pattern. For aluminum K emission spectra, the third order $K\alpha_1$ peak of titanium was used, together with the unresolved $K\alpha_{1,2}$ doublet of metallic aluminum. For silicon, the third order $K\alpha_1$ peak of chromium was employed, together with the silicon metal unresolved $K\alpha_{1,2}$ doublet. The recently available, revised X-ray wavelength tables of Bearden were used for all wavelength calibrations (Bearden, 1967).

Samples of minerals were selected to represent a range of framework and chain silicates as well as pyrosilicates and orthosilicates. The cordierite specimen from Guilford, Connecticut, was obtained through the courtesy of G. V. Gibbs and is the same material upon which

he has reported complete three-dimensional crystallographic data (Gibbs, 1966). The anorthite sample,[4] from Miyake, Japan, is similar to the material studied by Ribbe and Megaw (1962).

RESULTS

Typical X-ray emission spectra were shown in Figures 1, 2, 3, and 4 of a previous paper (Dodd, 1968a). The "diagram" lines and the distinguishable "non-diagram" or "satellite" lines of the $K\alpha$ and $K\beta$ series were labelled on Figure 1 of that publication on three spectra each for Mg, Al, and Si. Figure 1 of this paper displays only the $K\beta$-band spectra (including the $K\beta'$ satellites) for the silicon "standards," silicon metal, and fused silica glass, traced with faint lines, together with similar $K\beta$-band curves for two framework silicates, cordierite, and anorthite, and two
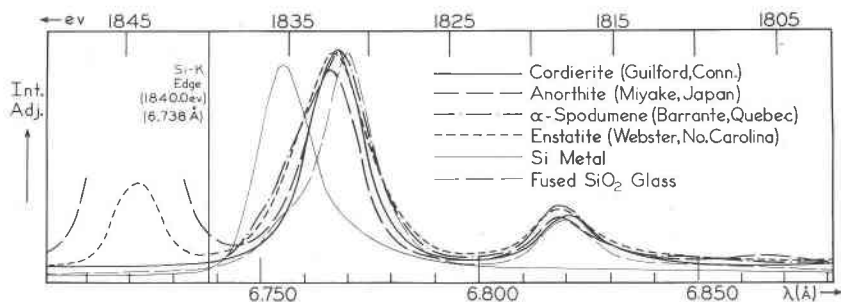

FIG. 1. Silicon $K\beta$-band X-ray emission spectra of framework silicates, together with the silicon spectral references, silicon metal, and fused silica (20 keV, ADP crystal).

chain silicates, α-spondumene and enstatite. With respect to the SiO_2 reference "standard," it was found in previous work that the *main* $K\beta$-band peaks of cristobalite, tridymite, quartz, and fused silica glass were coincident within the limits of resolution of the electron microprobe spectrometers used. Similar results were obtained by Läuger using a high resolution spectrometer (Läuger, 1968).

Figure 2 presents silicon $K\beta$-band spectra for the pyrosilicate (Si_2O_7-type) structures, thortveitite, and gehlenite, as well as a similar spectrum for the Si_6O_{18} framework silcate beryl (Gibbs, 1968). Representative orthosilicates, structures with isolated SiO_4 groups, were used to obtain the spectra shown in Figure 3 for olivine, monticellite, zircon, and pyrope garnet. The zircon spectrum includes the zirconium Ll band, the wavelength of which is so close to that of the Si $K\beta$ band that it cannot be eliminated by pulse height discrimination. Other spectral lines seen in Figures 1, 2, and 3 include the second order peak of Ca-$K\alpha_{1,2}$ in the

[4] Obtained from the University of Michigan Museum through the courtesy of D. R. Peacor.

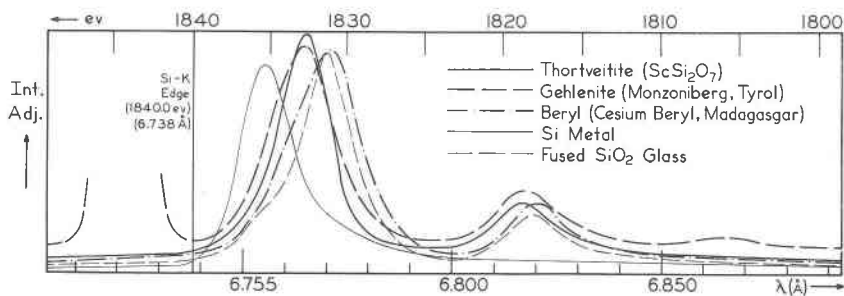Fig. 2. Silicon Kβ-band X-ray emission spectra of pyrosilicates, the framework
silicate, beryl, and the silicon references (20 keV, ADP crystal).

spectra of anorthite and enstatite in Figure 1, in the spectrum of gehlenite
in Figure 2, and in the spectrum of monticellite in Figure 3. With proper
pulse height discrimination it is possible to eliminate the appearance of
this latter doublet peak for the enstatite sample used, but the larger
concentrations of calcium make it essentially impossible to eliminate
completely for the other three minerals. Finally, on the anorthite spec-
trum in Figure 1 and the gehlenite spectrum in Figure 2 the weak
strontium Lα1 and Lα2 peaks can be seen. These, also, cannot be elim-
inated by pulse height discrimination because they lie too close to the
Kβ-band.

Figures 4 and 5 display aluminum Kβ-band spectra of many of the
same silicates for which the Si Kβ spectra are shown in Figures 1, 2, and
3. The Al Kβ-band spectra of the framework silicates cordierite, anorthite
and microcline, and the chain silicate, α-spodumene, are shown in Figure
4. In these structures Al substitutes for Si in TO_4 tetrahedra in a more or
less ordered manner. Finally, in Figure 5 the Kβ-band spectra of pyrope
garnet and beryl are reproduced. In both Figures 4 and 5 the reference
spectra in fine lines are those of aluminum metal and α-Al_2O_3. In previous
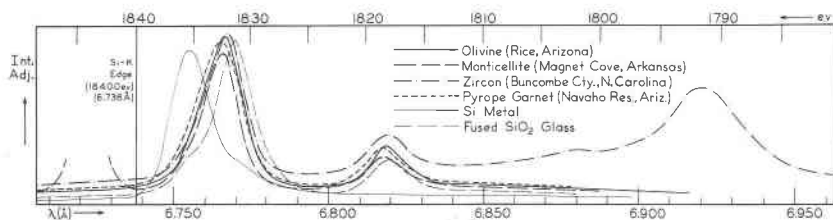work it was found that the Kβ-band spectra of naturally occurring

Fig. 3. Silicon Kβ-band X-ray emission spectra of orthosilicates, together with
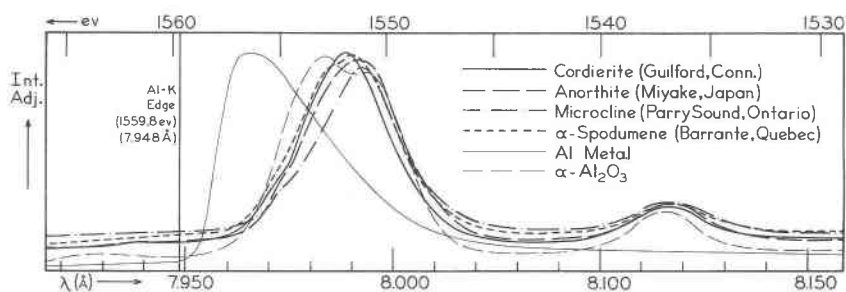silicon references (20 keV, ADP crystal).

FIG. 4. Aluminum Kβ-band X-ray emission spectra of framework silicates, α-spodumene and the aluminum spectral references aluminum metal and α-Al₂O₃ (20 keV and ADP crystal).

corundum minerals, of synthetic single crystal sapphire and ruby, and of the polycrystalline ceramic, α-Al₂O₃, were essentially coincident.

Discussion

The results of initial interpretations based on MO theory have been encouraging for both X-ray absorption spectra (Glen, 1968) and X-ray emission spectra (Dodd, 1968a). The main Kβ-band peak observed in spectra of magnesium, aluminum, and silicon oxides has been designated as a M-K electronic transition (Bearden, 1967). The MO interpretation of the Kβ-band spectra of these elements is based on the assumption that the principal peak in the Kβ-band may be ascribed to a $3p$-$1s$ electronic transition. This basic assumption appears well justified because $3p$-$1s$ transitions obey all selection rules for electronic dipole radiation. In addition, steric factors involving the relative orientation and degree of orbital overlap on metal and oxygen atomic sites in known silicate crystal structures must be considered.
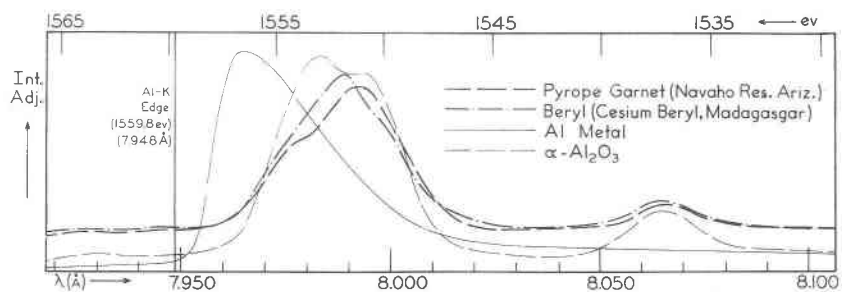

FIG. 5. Aluminum Kβ-band X-ray emission spectra of gehlenite, pyrope garnet, and beryl, together with aluminum references (20 keV, ADP crystal).

For TO$_4$ tetrahedra in silicates a tentative MO energy level diagram is presented in Figure 6. The diagram is essentially identical to one proposed by Cruickshank (1961) for SiO$_2$.

The relative energy levels in the diagram, shown in Figure 6, are presumed to be only qualitatively correct, but the diagram serves the purpose required for spectral interpretation. The major peak observed in Kβ-band spectra of silicates and aluminosilicates is assumed to result from a 3p-1s transition. Furthermore, in the case of tetrahedrally-coordinated third period oxides the only 3p orbitals populated with electrons are the 3$p(\sigma)$-bonding orbitals having group t_2 symmetry. Therefore, the major Kβ-band peak for Al and Si tetrahedrally-coordinated oxides must be assigned to a 3$p(\sigma^b)$-1s transition. It is not possible to have $p\pi$ bonding in oxides with tetrahedral symmetry, hence the major peak for the Al and Si in TO$_4$ tetrahedra of silicates and aluminosilicates should involve 3$p\sigma$ electronic transitions only.
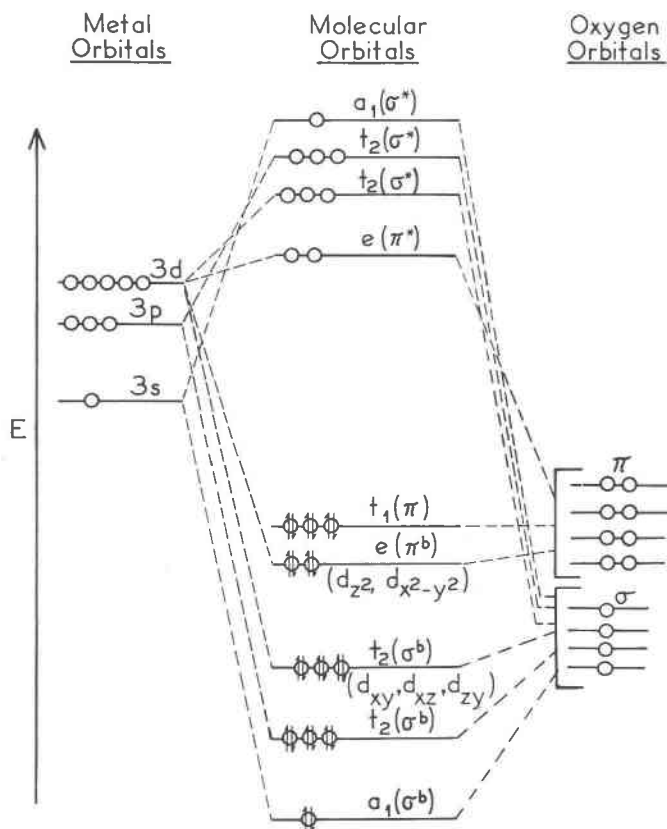

FIG. 6. Relative orbital energies in TO$_4$ tetrahedra in silicates and aluminosilicates.

In the Kβ-band spectrum of Si in fused SiO$_2$ (and quartz) shown in Figures 2, 4, and 5 an unresolved, weaker, high-energy peak can be seen in addition to the main Kβ peak. This high energy SiO$_2$ peak is seen distinctly in the high resolution spectral data of Läuger (1968). If the intense Si Kβ-band peak is attributed to a $3p(\sigma^b)$-$1s$ transition, as it must be on the basis of the argument outlined above, the unresolved higher energy peak must be assigned to a forbidden (or quadrupole) transition involving a π-bonding orbital having either group e or t_2 symmetry. On the basis of the argument presented by Cruickshank (1961), we prefer to assign this unresolved high energy peak to a $3d(\pi^b)$-$1s$ transition involving the Si d-orbitals, $d_{x^2-y^2}$ and d_{y^2}. Cruickshank pointed out that these orbitals, having group e symmetry, are in a position to participate in π-bonding with $2p\pi$ orbitals of oxygen in silica and many silicates. Cruickshank also commented that this d-$p\pi$-bonding probably results in the observed covalent nature of the double bond in silica and the concommitant shortening of the Si-O single bond distance. Corroboration for the assignment of this peak to a $3d(\pi^b)$-$1s$ transition rather than to a $3d$ (σ^b)-$1s$ transition has been found in a recent X-ray absorption study of transition metal complexes.[5]

Referring again to Figures 1, 2, and 3, the high energy $3d(\pi^b)$-$1s$ transition peak is seen, although not resolved distinctly, on the SiO$_2$ Kβ-band. The corresponding spectral curves for cordierite, anorthite, α-spondumene, and enstatite, shown in Figure 1, do not exhibit a similar peak. If it is present it must be exceedingly weak. We would expect that higher resolution spectra might resolve it. It is of interest, however, to note the apparent occurrence of weak aluminum $3d(\pi^b)$-$1s$ peaks in the Al Kβ-band spectra of the framework silicates cordierite, anorthite, and microcline, shown in Figure 4. In the longer wavelength region of the Al Kβ-band spectra the ADP analyzing crystal used had greater dispersion than for the shorter wavelength Si Kβ-band region. This difference in dispersion may account for the failure to observe corresponding peaks in Figure 1. On the basis of the p-d π-bonding theory of Cruickshank (1961), one would expect similar Si-O bonding and Al-O bonding in TO$_4$ tetrahedral coordination.

In addition to the framework silicate specimens whose spectra are shown on Figure 1, we have measured spectra of numerous other samples. These have included a group of other cordierite samples, and both the cordierites and feldspars have included samples representing varying

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[5] X-ray absorption measurements in our laboratory show that a sharp $1s$-$3d$ peak will occur in tetrahedral complexes only if the antibonding π orbitals, $3d_{x^2-y^2}$, and $3d_{z^2}$ are unoccupied. This absorption peak is briefly mentioned in a paper by Glen and Dodd (1968) and is the subject of a paper currently being prepared for publication.

states of order-disorder with respect to Si and Al in tetrahedral sites and varying extents of weathering. The measured main Si Kβ-band peak positions of these various cordierties have not coincided for all specimens with respect to their wavelength or spectral emergy positions. The poor reproducibility of Si Kβ-band peaks for different cordierite specimens has been assumed to be primarily the result of different degrees of sample alteration by weathering, which would result in significant but varying contribution of Si-OH bonds to the silicate spectra. Other experimental problems which may effect spectral reproducibility include perfection of the spectrometer analyzing crystal used and anomalous dispersion of the analyzing crystal (Parratt, 1954).

To some extent the main Si Kβ-band peak positions of the feldspar specimens also showed some scatter, but they were observed to coincide to a greater degree that the cordierites. Similar observations were made for the Al Kβ-band spectra of various cordierites and feldspars (see Fig. 4). The cordierite and anorthite specimens whose spectra are shown in Figures 1 and 4 were selected because they have been well characterized crystallographically by up-to-date 3-D single-crystal structural analysis (Gibbs, 1966; Ribbe, 1962).

In Figure 2 the Si Kβ-band peaks of the Si_2O_7 silicates thortveitite and gehlenite are seen to be shifted further to higher energies (relative to that of SiO_2) than those of the framework and chain silicates. Furthermore, the thortveitite and gehlenite peaks occur almost at the same energy or wavelength position in spite of the fact that one of the Si sites in each Si_2O_7 group is occupied by an Al atom in gehlenite. The main Si Kβ-band peak of beryl, on the other hand, is seen to occur at about the same wavelength as that of SiO_2 although the beryl peak is broader. This would imply that the Si-O bond stability in beryl is comparable to that in SiO_2, a conclusion that is consistent with the recent determination that beryl is a framework, rather than a ring, silicate (Gibbs, 1968).

In Figure 3, showing Kβ-band spectra of orthosilicates with isolated SiO_4 groups, it may be noted that the peaks of olivine ($> 80\%$ Mg_2 SiO_4), zircon ($ZrSiO_4$), monticellite ($MgCaSiO_4$), and pyrope garnet occur closely bunched at a spectral position intermediate between those of the Si_2O_7 silicates and silica and close to the Si Kβ-band peak positions of framework and chain silicates. This appears to indicate an intermediate degree of Si-O bend stability.

Figure 7 shows a tentative MO energy diagram for octahedrally co-ordinated Al in silicates. It is similar to one published earlier (Dodd, 1968a). Again, the relative energy levels are approximate and the relative order of the levels of anti-bonding orbitals might be changed if the re-
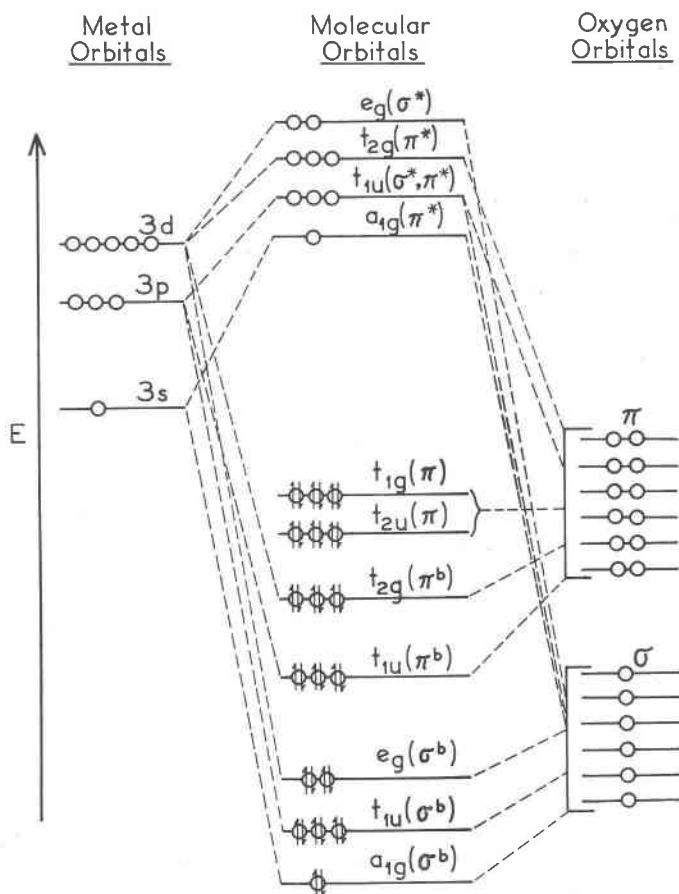
Fig. 7. Relative orbital energies in octahedrally coordinated aluminum.

quired computations were performed; but this would not affect the argument herein. The $3p\pi$ bonding orbitals of group t_{1u} symmetry, shown in Figure 7, are populated with electrons in the silicates studied in this paper. These orbitals lie at a higher energy level than the corresponding $3p\sigma$ bonding orbitals, also with t_{1u} symmetry. In a previous paper (Dodd, 1968a) we made the assumption that the higher peak observed in the $K\beta$-band of α-Al_2O_3 should be assigned to a $3p(\pi^b)$-$1s$ transition and that the lower energy peak should be assigned to a $3p(\sigma^b)$-$1s$ transition.

The Al $K\beta$-band spectra of pyrope garnet, shown in Figure 5, is more interesting than its corresponding Si $K\beta$ spectrum. The Al $K\beta$-band is clearly split into two peaks, with the higher energy peak having a lower

intensity. This weaker high energy peak must be assigned to a $3p$ (π^b)-$1s$ transition, following the same line of reasoning used in the interpretation of the α-Al$_2$O$_3$ spectrum. In pyrope garnet, two Al octahedra occur in four-member rings together with two Si tetrahedra. This interpretation of the garnet spectrum would imply some contribution of π-bonding to the Al-O bond in pyrope garnet. The measured Al Kβ-band spectrum of another pyrope garnet not illustrated in this paper (from heavy particle concentrate of Riverton Pipe, Kimberly, South Africa) was essentially identical to the measured spectrum of the Navaho Reservation, Arizona, specimen referred to above.

The Al Kβ-band of beryl (reproduced in Figure 5) is seen to be relatively broad and to lie at approximately the same energy level as the corresponding band in the framework silicates. For beryl, this peak must be attributed to a $3p(\sigma^b)$-$1s$ transition. Apparently the six-fold coordinated Al-O bonds in beryl are sufficiently distorted so that the orbitals are not properly aligned for $p\pi$ bonding.

Further interpretation of X-ray emission spectra based on the ideas discussed in this paper requires detailed analysis of the extent of orbital overlap for each Si-O and Al-O bond in each silicate structure. Quantitative determination of orbital overlap is complex. We suggest a qualitative or semi-quantitative estimate may be obtained by the use of silicate crystal structure models and appropriate atomic orbital models having their centers of symmetry located at the known atomic sites in the crystal models. With such models the extents of orbital overlap can be estimated visually. An example is the plate in Cruickshank's paper (Cruickshank, 1961) which shows the oxygen $2p\pi$ orbitals adjacent to silicon $d_{x^2-y^2}$ and d_{z^2} orbitals. The observed Kβ-band spectra may be studied with respect to band splitting and the discernible peaks assigned to specific transitions. In the silicates, relative Si-O and Al-O bond energies should be a function of degree of overlap and this, in turn, should be a function of both bond length and bond angle.

Elsewhere (Dodd, 1968b) we have described how experimental data such as that presented in Figures 1, 2, and 3 can be used to compare the energy of an average Si-O bond in a silicate glass to the energy of Si-O bonds in the framework structure of α-quartz. The degree of Si-O bond destabilization in a crystalline silicate, relative to that in quartz, may be estimated by measuring the difference in eV between the main Kβ-band spectral peak energies for the silicate and for quartz. If the silicate Si Kβ-band peak lies at a higher energy, the average silicate Si-O bond would be considered to be less stable than those in quartz. A measure of this destabilization is the measured energy difference. The method is based (1) on the use of the tetrahedral MO energy level diagram shown

in Figrun 6, (2) on the assumptions that the $1s$ orbital level is constant, and (3) that all bonding orbitals would be shifted to the same extent as the $3p\sigma^b$ orbitals, relative to the orbital energy levels in quartz. Rough quantitative estimates of relative destabilization energies based on this concept are presented in Table 1. The peak positions were estimated by extrapolating medians to the maximum intensity. Nevertheless, assuming one significant figure precision for the figures in the right hand column of Table 1, it is apparent that Si-O bonds in the framework silicate beryl are as stable as those in quartz; that the isolated SiO_4 tetrahedral ortho-silicates, the framework silicates, and the chain silcates all are destabilized to about the same degree; and that the Si_2O_7 double-tetrahedra, pyrosilicate structures have the weakest Si-O bonds of the silicates studied.

TABLE 1. ESTIMATED DECREASE IN STABILITY OF SI-O BONDS IN
SILICATES RELATIVE TO SI-O BONDS IN QUARTZ

Sample	Approx. Si Kβ-Band Main Peak Position (eV)	Displacement of Peak Relative to SiO_2 (eV)	Approx. Destabilization Energy of Si-O Bond[a] (kcal/mole)
Reference			
SiO_2 (Figs. 1, 2, and 3)	1831.3	—	—
Framework Silicates			
Cordierite (Fig. 1)	1832.2	−0.9	−21
Anorthite (Fig. 1)	1832.4	−1.1	−25
Beryl (Fig. 2)	1831.3	0	0
Chain Silicates (Fig. 1)			
α-spodumene	1831.8	−0.5	−12
Enstatite	1832.5	−1.2	−28
Si_2O_7 Silicates (Fig. 2)			
Thortveitite	1832.8	−1.5	−35
Gehlenite	1832.8	−1.5	−35
Orthosilicates (Fig. 3)			
Zircon	1832.0	−0.7	−16
Olivine	1832.2	−0.9	−21
Monticellite	1832.3	−1.0	−23
Pyrope Garnet	1832.5	−1.2	−28

[a] The precision of the measured destabilization Si-O bond energy should not be taken as better than one significant figure, although two are reported in this column.

Summary

Kβ-band x-ray emission spectra of selected silicates and alumino-silicates have been measured and interpreted with the help of MO theory. Band splitting of the measured Kβ-band spectra has been related to specific electronic transition assignments. The measured wavelength, or corresponding spectral energy of the main Si Kβ-band peaks, have been used as a measure of the relative destabilization of Si-O bonds in particular silicate minerals relative to the strength of Si-O bonds in fused SiO_2 or quartz.

The mineral beryl was found to have about the same Si-O bond strength as SiO_2. The Si-O bond strength of other framework silicates was judged to be less than SiO_2 and beryl but about the same as the chain silicates and orthosilicates studied. The Si-O bonds of the pyrosilicates were found to be the least stable.

Aluminum Kβ-band spectra of specimens of pyrope garnet from two localities were interpreted in a manner that indicates a π-bonding contribution to the Al-O bonds.

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