

## A SURVEY OF CHEMICAL BONDING IN SILICATE MINERALS BY X-RAY EMISSION SPECTROSCOPY<sup>1,2</sup>

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### ABSTRACT

A survey has been made of the  $K\beta$ -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  $K\beta$ -band spectra of tetrahedrally coordinated Al proxying for Si, in both ordered and disordered structures, were found to be similar to the Si  $K\beta$ -band spectra 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

<sup>1</sup> Research sponsored jointly by Owens-Illinois, Inc. and the Air Force Office of Scientific Research, Directorate of Chemical Science, under Contract No. AF49(638)1670.

<sup>2</sup> Paper presented at the Annual Meeting of the Geological Society of America and associated societies, Mexico City, November 11, 1968.

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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  $\pi$ -bonding in these oxides and relate the stability of Si-O and Al-O bonds in specific structures to similar bonds in  $\text{SiO}_2$  and  $\alpha\text{-Al}_2\text{O}_3$ , 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- $\mu\text{m}$  and 1/4- $\mu\text{m}$  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 defocused to cross-sections as large as 200- to 300- $\mu\text{m}$  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 defocused 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- $\mu\text{m}/\text{min}$ . 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,<sup>4</sup> 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

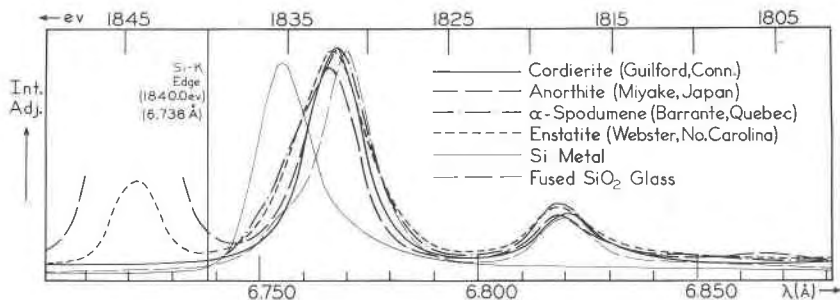


FIG. 1. Silicon  $K\beta$ -band X-ray emission spectra of framework silicates, together with the silicon spectral references, silicon metal, and fused silica (20 keV, ADP crystal).

chain silicates,  $\alpha$ -spodumene and enstatite. With respect to the  $\text{SiO}_2$  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 Lauser using a high resolution spectrometer (Lauser, 1968).

Figure 2 presents silicon  $K\beta$ -band spectra for the pyrosilicate ( $\text{Si}_2\text{O}_7$ -type) structures, thortveitite, and gehlenite, as well as a similar spectrum for the  $\text{Si}_6\text{O}_{18}$  framework silicate beryl (Gibbs, 1968). Representative orthosilicates, structures with isolated  $\text{SiO}_4$  groups, were used to obtain the spectra shown in Figure 3 for olivine, monticellite, zircon, and pyrope garnet. The zircon spectrum includes the zirconium L1 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  $\text{Ca-K}\alpha_{1,2}$  in the

<sup>4</sup> Obtained from the University of Michigan Museum through the courtesy of D. R. Peacor.

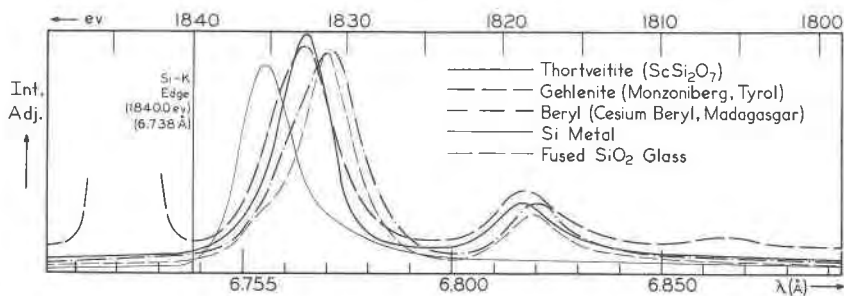


FIG. 2. Silicon  $K\beta$ -band X-ray emission spectra of pyrosilicates, the framework silicate, beryl, and the silicon references (20 keV, ADP crystal).

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 spectrum in Figure 1 and the gehlenite spectrum in Figure 2 the weak strontium  $L\alpha_1$  and  $L\alpha_2$  peaks can be seen. These, also, cannot be eliminated by pulse height discrimination because they lie too close to the  $K\beta$ -band.

Figures 4 and 5 display aluminum  $K\beta$ -band spectra of many of the same silicates for which the Si  $K\beta$  spectra are shown in Figures 1, 2, and 3. The Al  $K\beta$ -band spectra of the framework silicates cordierite, anorthite and microcline, and the chain silicate,  $\alpha$ -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  $K\beta$ -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  $\alpha$ - $Al_2O_3$ . In previous work it was found that the  $K\beta$ -band spectra of naturally occurring

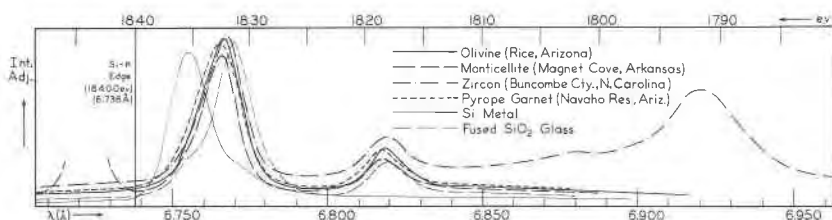


FIG. 3. Silicon  $K\beta$ -band X-ray emission spectra of orthosilicates, together with silicon references (20 keV, ADP crystal).

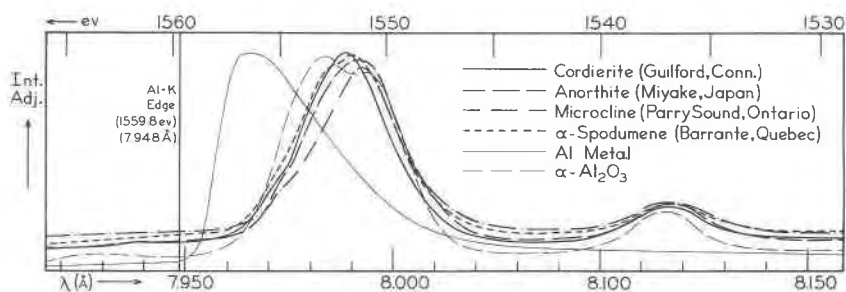


FIG. 4. Aluminum  $K\beta$ -band X-ray emission spectra of framework silicates,  $\alpha$ -spodumene and the aluminum spectral references aluminum metal and  $\alpha$ - $Al_2O_3$  (20 keV and ADP crystal).

corundum minerals, of synthetic single crystal sapphire and ruby, and of the polycrystalline ceramic,  $\alpha$ - $Al_2O_3$ , 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  $K\beta$ -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  $K\beta$ -band spectra of these elements is based on the assumption that the principal peak in the  $K\beta$ -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.

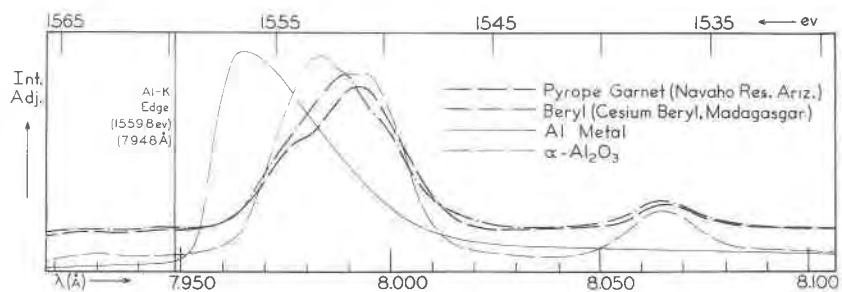


FIG. 5. Aluminum  $K\beta$ -band X-ray emission spectra of gehlenite, pyrope garnet, and beryl, together with aluminum references (20 keV, ADP crystal).

For  $\text{TO}_4$  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  $\text{SiO}_2$ .

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  $\text{K}\beta$ -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  $3p(\sigma)$ -bonding orbitals having group  $t_2$  symmetry. Therefore, the major  $\text{K}\beta$ -band peak for Al and Si tetrahedrally-coordinated oxides must be assigned to a  $3p(\sigma^b)$ - $1s$  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  $\text{TO}_4$  tetrahedra of silicates and aluminosilicates should involve  $3p\sigma$  electronic transitions only.

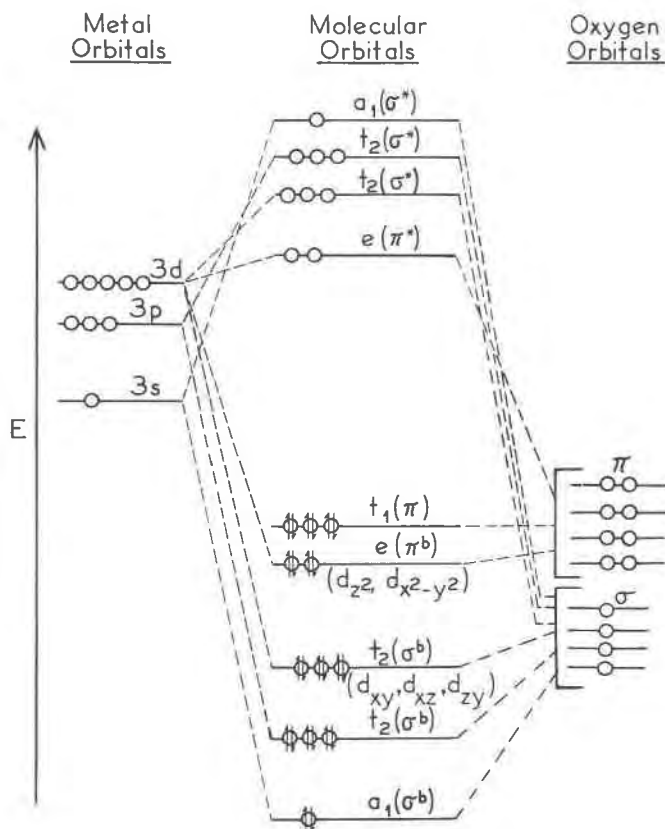


FIG. 6. Relative orbital energies in  $\text{TO}_4$  tetrahedra in silicates and aluminosilicates

In the  $K\beta$ -band spectrum of Si in fused  $\text{SiO}_2$  (and quartz) shown in Figures 2, 4, and 5 an unresolved, weaker, high-energy peak can be seen in addition to the main  $K\beta$  peak. This high energy  $\text{SiO}_2$  peak is seen distinctly in the high resolution spectral data of Lauger (1968). If the intense Si  $K\beta$ -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  $\pi$ -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  $\pi$ -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 concomitant 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  $3d(\sigma^b)$ - $1s$  transition has been found in a recent X-ray absorption study of transition metal complexes.<sup>5</sup>

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  $\text{SiO}_2$   $K\beta$ -band. The corresponding spectral curves for cordierite, anorthite,  $\alpha$ -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  $K\beta$ -band spectra of the framework silicates cordierite, anorthite, and microcline, shown in Figure 4. In the longer wavelength region of the Al  $K\beta$ -band spectra the ADP analyzing crystal used had greater dispersion than for the shorter wavelength Si  $K\beta$ -band region. This difference in dispersion may account for the failure to observe corresponding peaks in Figure 1. On the basis of the  $p$ - $d$   $\pi$ -bonding theory of Cruickshank (1961), one would expect similar Si-O bonding and Al-O bonding in  $\text{TO}_4$  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

<sup>5</sup> X-ray absorption measurements in our laboratory show that a sharp  $1s$ - $3d$  peak will occur in tetrahedral complexes only if the antibonding  $\pi$  orbitals,  $3d_{x^2-y^2}$ , and  $3d_{y^2}$  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  $K\beta$ -band peak positions of these various cordierites have not coincided for all specimens with respect to their wavelength or spectral energy positions. The poor reproducibility of Si  $K\beta$ -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  $K\beta$ -band peak positions of the feldspar specimens also showed some scatter, but they were observed to coincide to a greater degree than the cordierites. Similar observations were made for the Al  $K\beta$ -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  $K\beta$ -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  $K\beta$ -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  $K\beta$ -band spectra of orthosilicates with isolated  $SiO_4$  groups, it may be noted that the peaks of olivine ( $>80\%$   $Mg_2SiO_4$ ), 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  $K\beta$ -band peak positions of framework and chain silicates. This appears to indicate an intermediate degree of Si-O bond stability.

Figure 7 shows a tentative MO energy diagram for octahedrally coordinated 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-



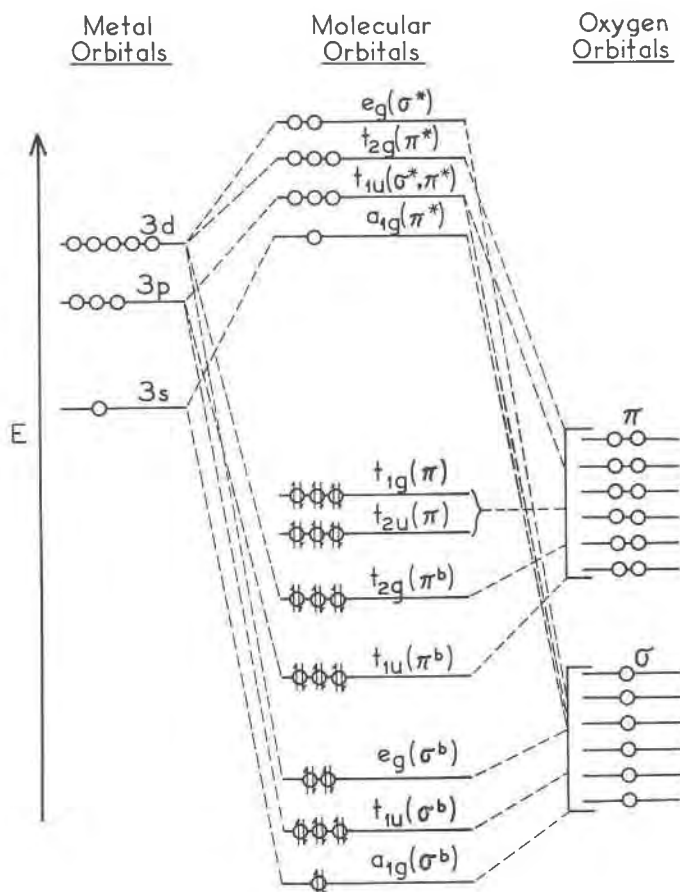


Fig. 7. Relative orbital energies in octahedrally coordinated aluminum.

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  $\alpha\text{-Al}_2\text{O}_3$  should be assigned to a  $3p(\pi^b)\text{-}1s$  transition and that the lower energy peak should be assigned to a  $3p(\sigma^b)\text{-}1s$  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  $3p(\pi^b)-1s$  transition, following the same line of reasoning used in the interpretation of the  $\alpha\text{-Al}_2\text{O}_3$  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  $\pi$ -bonding to the Al-O bond in pyrope garnet. The measured Al  $K\beta$ -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  $K\beta$ -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  $K\beta$ -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  $\alpha$ -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  $K\beta$ -band spectral peak energies for the silicate and for quartz. If the silicate Si  $K\beta$ -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 Figure 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  $\text{SiO}_4$  tetrahedral orthosilicates, the framework silicates, and the chain silicates all are destabilized to about the same degree; and that the  $\text{Si}_2\text{O}_7$  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 $K\beta$ -Band Main Peak Position (eV)	Displacement of Peak Relative to $\text{SiO}_2$ (eV)	Approx. Destabilization Energy of Si-O Bond <sup>a</sup> (kcal/mole)
Reference			
$\text{SiO}_2$ (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)			
$\alpha$ -spodumene	1831.8	-0.5	-12
Enstatite	1832.5	-1.2	-28
$\text{Si}_2\text{O}_7$ 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

<sup>a</sup> 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

K $\beta$ -band x-ray emission spectra of selected silicates and aluminosilicates have been measured and interpreted with the help of MO theory. Band splitting of the measured K $\beta$ -band spectra has been related to specific electronic transition assignments. The measured wavelength, or corresponding spectral energy of the main Si K $\beta$ -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<sub>2</sub> or quartz.

The mineral beryl was found to have about the same Si-O bond strength as SiO<sub>2</sub>. The Si-O bond strength of other framework silicates was judged to be less than SiO<sub>2</sub> 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 K $\beta$ -band spectra of specimens of pyrope garnet from two localities were interpreted in a manner that indicates a  $\pi$ -bonding contribution to the Al-O bonds.

## ACKNOWLEDGMENTS

We wish to acknowledge the cooperation of Professor W. C. Bigelow and Mr. Frank Drogosz of the Department of Chemical and Metallurgical Engineering of the University of Michigan, Ann Arbor, who made available to us, and assisted in maintaining, the electron microprobe used in this work. Further thanks are due Professor G. V. Gibbs of Virginia Polytechnic Institute who read the manuscript critically and who presented the paper for us at the Mexico City G.S.A. meeting. Numerous discussions with Professor Gibbs, Mr. Gordon Brown, and Professor P. H. Ribbe of V.P.I. have been especially appreciated. Mineral samples were obtained through the courtesy of Professors D. R. Peacor and E. W. Heinrich of the University of Michigan, from Professor G. V. Gibbs, and from Professor J. T. Wilband of the University of Toledo.

## REFERENCES

- BEARDEN, J. A. (1967) X-ray wavelengths, *Rev. Mod. Phys.* **39**, 98-124.
- CRUICKSHANK, D. W. J. (1961), The role of 3d-orbitals in  $\pi$ -bonds between (a) silicon, phosphorus, sulphur, or chlorine and (b) oxygen or nitrogen. *J. Chem. Soc. (London)* **1961**, Part IV, 5486-5504.
- DODD, C. G. AND G. L. GLEN (1968a) Chemical bonding studies of silicates and oxides by X-Ray K-emission spectroscopy *J. Appl. Phys.* **39**, 5377-5384.
- AND ——— (1968b) Chemical bonding in glasses by X-Ray emission spectroscopy. *Amer. Ceram. Soc. Meet. Chicago, Ill., April 22, 1968*.
- GIBBS, G. V. (1966) The polymorphism of cordierite, I: The crystal structure of low cordierite. *Amer. Mineral.* **51**, 1068-1087.
- , D. W. BRECK, AND E. P. MEAGHER (1968) Structural refinement of hydrous and anhydrous synthetic beryl, Al<sub>2</sub>(Be<sub>2</sub>Si<sub>6</sub>)O<sub>18</sub>, and emerald Al<sub>1.9</sub>Cr<sub>0.1</sub>(Be<sub>3</sub>Si<sub>6</sub>)O<sub>18</sub>. *Lithos* **1**, 275-285.
- GLEN, G. L. AND C. G. DODD (1968) Use of Molecular orbital theory to interpret X-ray K-absorption spectral data. *J. Appl. Phys.* **39** 5372-5377.

- LÄUGER, K. (1968) *Über den Einfluss der Bindungsart und der Kristallstruktur auf das K-Röntgen emission-spektrum von Aluminium und Silizium*. Diss. Ludwig-Maximilians-Univ., München, Germany.
- PARRATT, L. G. AND C. F. HEMPSTEAD (1954) Anomalous dispersion and scattering of X rays *Phys. Rev.* **94**, 1593-1600.
- RIBBE, P. H. AND H. D. MEGAW (1962) The structure of transitional anorthite: A comparison with primitive anorthite. *Norsk Geol. Tidssk.* **42**, 158-167.

*Manuscript received April 7, 1969; accepted for publication June 30, 1969.*