Silicon and silicon dioxide K x-ray spectra from hydrogen, helium, and oxygen bombardment

Joseph McWherter, David K. Olsen, Herman H. Wolter, and C. Fred Moore
Center for Nuclear Studies, The University of Texas at Austin, Austin, Texas 78712
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Silicon and silicon dioxide K x-ray spectra produced by 0.8-MeV hydrogen, 3.2-MeV helium, and 13.0- and 35.0-MeV oxygen bombardment were measured with a high-resolution crystal spectrometer. The resulting $K\alpha$ and $K\beta$, diagram and satellite, chemical energy shifts observed with these ions and those from electron excitation are compared and discussed. In general, the chemical shifts obtained from the different projectiles are similar and are dependent upon the amount of additional L-shell ionization. However, the oxygen-produced $K\beta$ satellite shifts are anomalously large. The spectra indicate that perhaps these shifts are due to transitions from the conduction band of silicon dioxide.

I. INTRODUCTION

It has been known for many years that x-ray emission spectra are sensitive to the chemical environment of the emitting atom.[1] In particular, photon and electron bombardment of molecules has shown that chemical bonding causes the inner-shell, diagram x-ray lines to be shifted slightly in energy. Somewhat larger chemical energy shifts, which are defined to be the x-ray energy of the compound minus that of the metal, have been measured for the weak satellite transitions of these diagram lines, whereas very large chemical shifts have been measured for transitions originating from the valence shells. In recent years it has been established that both light- and heavy-ion bombardment produces enhanced x-ray satellite intensities with respect to photon and electron excitation.[2] This increased satellite yield facilitates the study of chemical shifts from such transitions.

Some work has been reported on chemical effects of x-ray spectra produced by ion bombardment.[3,4] In particular, Burkhalter, Knudson, Nagel, and Dunning[4] have measured the energy shifts between Al and Al_2O_3, diagram and satellite lines produced by 5.0-MeV helium and neon bombardment. In the present work chemical effects between Si and SiO_2, $K\alpha$ and $K\beta$ x-ray spectra produced by 0.8-MeV hydrogen, 3.2-MeV helium, and 13.0- and 35.0-MeV oxygen bombardment were investigated. We find that recoil effects are not a severe problem with oxygen bombardment at these energies, and that hydrogen, helium, and oxygen excitation give $K\alpha$ chemical shifts similar to the positive shifts produced by electron bombardment.[5] However, for satellite transitions from high L-shell ionization, which were only produced by helium and oxygen bombardment, negative $K\alpha$ energy shifts are observed. Similar to Burkhalter *et al.*,[4] we find some $K\beta$ energy shifts to be very large and positive. Our measurements indicate that perhaps these anomalously large $K\beta$ shifts are caused by x-ray transitions from excited bands in SiO_2 which are normally empty.

II. EXPERIMENTAL APPARATUS

The x-ray spectra were produced from bombardment with 0.8-MeV proton and 3.2-MeV α particles from the University of Texas KN single-stage Van de Graaff and 13.0-, 30.0-, and 35.0-MeV oxygen ions from the University of Texas EN Tandem Van de Graaff accelerator. These ions were incident at 45° on to thick targets and the resultant x rays were wavelength analyzed by a reflection-type Bragg-crystal spectrometer mounted 90° to the beam direction and sharing a common vacuum with the beam line. Initially spectra were taken using an ammonium-dihydrogen-phosphate (ADP) crystal ($2d = 10.64$ Å); however later measurements employed an ethylenediamine D-tartrate (EDDT) crystal ($2d = 8.008$ Å) which resulted in better energy resolution.

The data collecting system was automated and controlled by a Digital Equipment Corporation PDP-7 on-line computer. After the spectrometer was set at an initial Bragg angle, the computer stepped the Bragg angle at equal-time intervals using a stepping motor and accumulated counts from a flow proportional counter that detected the diffracted x rays. Great care was taken to maintain constant beam current. Each spectrum is the sum of several scans. Thick wafers of 99.99% Si metal and 99.99% amorphous SiO_2 were used as targets. Each target was etched before scanning in order to reduce contamination. The total energy resolution (full width at half-maximum) measured for the oxygen-produced $K\alpha$ diagram

line was 2.4 eV for the ADP crystal and 2.0 eV for the EDDT crystal.

III. EXPERIMENTAL RESULTS

A. Hydrogen bombardment

Figure 1 shows the K x-ray spectra of Si and SiO_2 produced by hydrogen bombardment. The x-ray intensities from the SiO_2 target are roughly one-half of those from the Si target. In the $K\alpha$ wavelength region, the $K\alpha_{1,2}$ parent doublet is the most intense line followed by the KL satellite multiplet ($K\alpha'$, $K\alpha_3$, and $K\alpha_4$ lines) and the KL^2 multiplet ($K\alpha_5$ and $K\alpha_6$ lines). The KL^3 multiplet was only very weakly excited. In addition to the usual diagram $K\beta$ band, only the KL multiplet of the $K\beta$ satellites was observed. Several of the above x-ray lines have also been observed by Baun and Fischer[5] using electron excitation. The loss of intensity in SiO_2 prevented Baun and Fischer[5] from observing the $K\alpha'$, $K\alpha_5$, and $K\alpha_6$ lines for the compound. Furthermore, Baun and Fischer[5] were unable to observe the first satellite $K\beta$ multiplet from either the Si or SiO_2 target. We observe three lines in this multiplet from the SiO_2 target and only two lines from Si.

Table I lists the experimental energies for the lines produced from hydrogen and helium bombardment and those obtained by Baun and Fischer.[5] The listed energies are those which occur at the maximum intensity for the line. The chemical energy shifts for these x rays are also included in Table I and are believed to be accurate to ±0.2 and ±0.4 eV for the $K\alpha$ and $K\beta$ lines, respectively. No target self-absorption or crystal-reflection corrections where applied to the spectra because the chemical shifts are insensitive to these effects. The results indicate that the energy shifts from hydrogen bombardment are quite similar to those from electron bombardment. In

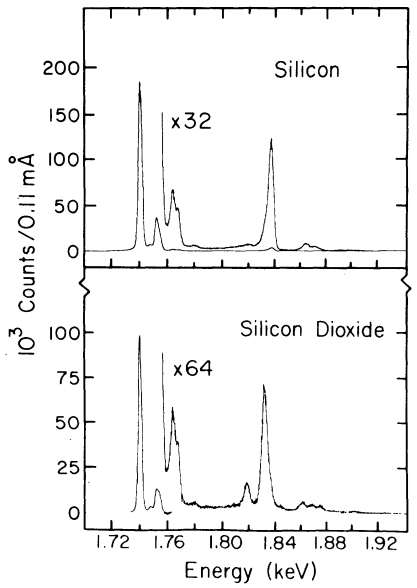

FIG. 1. Silicon and silicon dioxide K x-ray spectra produced from 0.8-MeV hydrogen bombardment. The strongest lines at 1.739 and 1.836 keV are the Si diagram $K\alpha$ and $K\beta$ transitions, respectively. Except for the $K\beta'$ transition at 1818 eV on the silicon-dioxide spectrum, the remaining lines are satellite transitions due to one and two additional L-shell vacancies. The energies of the peak maxima are listed in Table I.

TABLE I. X-ray energies and energy shifts from 7.0-keV electron, 0.8-MeV proton, and 3.2-MeV helium bombardment of Si and SiO_2.

Initial vacancies	x-Ray transition	x-Ray energy (eV) Electron[a] Si	Electron[a] SiO_2	Proton Si	Proton SiO_2	Helium Si	Helium SiO_2	Energy shift (eV) Electron[a]	Proton	Helium	HFS
K	$K\alpha_{1,2}$	1739.4	1739.9	1739.8	1740.3	1739.6	1740.2	+0.5	+0.5	+0.6	+0.4
KL	$K\alpha'$	1746.0	•••	1746.4	1747.6	1746.1	1747.0	•••	+1.2	+0.9	+0.8
KL	$K\alpha_3$	1750.5	1751.6	1750.8	1752.1	1750.9	1752.2	+1.1	+1.3	+1.3	+0.8
KL	$K\alpha_4$	1752.4	1753.2	•••	•••	•••	•••	+0.8	•••	•••	+0.8
KL^2	$K\alpha_5$	1762.3	•••	1762.5	1763.5	1762.7	1763.7	•••	+1.0	+1.0	+1.2
KL^2	$K\alpha_6$	1766.0	•••	1766.3	1767.0	1766.2	1766.7	•••	+0.7	+0.5	+1.2
KL^3	$K\alpha$	•••	•••	•••	•••	1778.4	1778.4	•••	•••	+0.0	+1.7
KL^4	$K\alpha$	•••	•••	•••	•••	1793.3	1793.2	•••	•••	−0.1	+2.2
K	$K\beta'$	•••	1817.8	•••	1818.1	•••	1818.3	•••	•••	•••	•••
K	$K\beta$	1835.9	1831.6	1835.8	1831.7	1835.6	1832.8	−4.3	−4.1	−2.8	−4.2
KL	$K\beta''$	1863.9	•••	1863.3	1861.0	1863.7	1861.3	•••	−2.3	−2.4	•••
KL	$K\beta'''$	1869.9	•••	1870.2	1868.4	1869.4	1867.8	•••	−1.8	−1.6	−3.0
KL	$K\beta$	•••	•••	•••	1874.3	•••	1874.0	•••	•••	•••	•••
KL^2	$K\beta$	•••	•••	•••	•••	1892.4	1890.8	•••	•••	−1.6	−1.8
KL^2	$K\beta$	•••	•••	•••	•••	1901.9	1901.7	•••	•••	−0.2	−1.8

[a]Reference 5.

particular a large negative energy shift of −4.1 eV was measured for the $K\beta$ diagram band and is due mainly to the increased bonding of the valence band of SiO_2. Furthermore, with hydrogen bombardment energy shifts for the $K\alpha_5$ and $K\alpha_6$ lines and the $K\beta$ multiplet from one additional L-shell vacancy were obtained. The $K\alpha$ and $K\beta$ energy shifts of Table I are shown in Figs. 2 and 3, respectively, where the abscissa is the number of additional L-shell vacancies in the initial state. When energy shifts were obtained for two lines of the same satellite multiplet, the energy shift of the most intense line is shown in the figures.

B. Helium bombardment

As shown in Fig. 4, the helium-produced Si and SiO_2 spectra show more intense satellite structure than the hydrogen-produced spectra. The multiplet structure is generally the same as for hydrogen excitation except that the SiO_2 lines exhibit less distinct splittings than the metal counterparts. K x-ray energies and energy shifts from these spectra are listed in Table I and shown in Figs. 2 and 3. The low-ionization, $K\alpha$ satellite lines have positive energy shifts similar to those obtained for hydrogen and electron bombardment. In addition, with helium ions we clearly observe

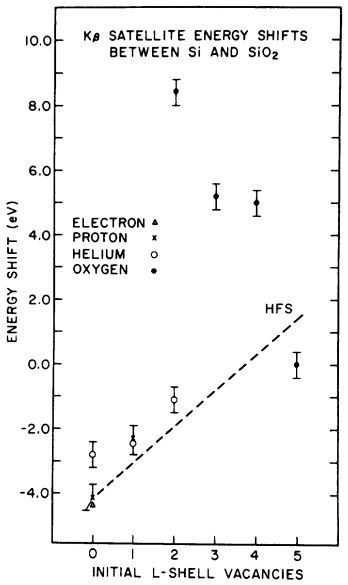

FIG. 3. Silicon $K\beta$ parent and satellite chemical peak energy shifts between Si and SiO_2 observed with electron, 0.8-MeV hydrogen, 3.2-MeV helium, and 13.0-MeV oxygen bombardment. The energy shift of the strongest line in each satellite multiplet is shown. The dashed line shows HFS calculated energy shifts in which the bonding of SiO_2 was simulated by removing one M-shell electron from Si.

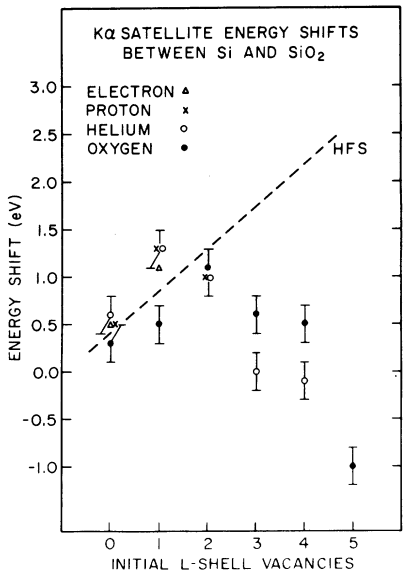

FIG. 2. Silicon $K\alpha$ parent and satellite chemical peak energy shifts between Si and SiO_2 observed with electron, 0.8-MeV hydrogen, 3.2-MeV helium, and 16.0-MeV oxygen bombardment. The energy shift of the strongest line in each satellite multiplet is shown. The dashed line shows Hartree-Fock-Slater-calculated energy shifts in which the bonding of SiO_2 was simulated by removing one M-shell electron from Si.

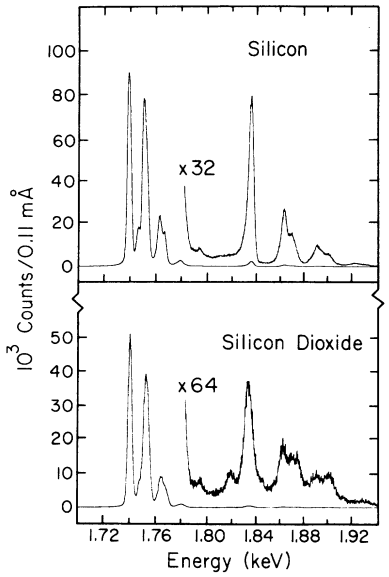

FIG. 4. Silicon and silicon dioxide K x-ray spectra produced from 3.2-MeV helium bombardment. The strongest lines at 1.739 and 1.836 keV are the Si diagram $K\alpha$ and $K\beta$ transitions, respectively. Satellite multiplets are observed with up to four additional L-shell vacancies, for $K\alpha$ transitions and two additional L-shell vacancies for $K\beta$ transitions. The energies of the peak maxima are listed in Table I.

the KL^3 and KL^4 satellite multiplets. These multiplets have chemical shifts of 0.0 and −0.1 eV, respectively. The maximum $K\alpha$ energy shift occurs for the $K\alpha_3$ line of the KL multiplet. Helium bombardment produces an unexpected and unexplained shift of only −2.8 eV for the diagram $K\beta$ band. Similar to hydrogen bombardment, with helium bombardment we observe three lines in the KL multiplet from SiO_2 and only two lines from Si. This additional line associated with valance transitions from SiO_2 is not observed in the KL^2 multiplet.

C. Oxygen bombardment

Spectra produced by 13.0- and 35.0-MeV oxygen bombardment are shown in Figs. 5 and 6, respectively. The oxygen bombardment produces spectra which are completely dominated by satellite structure, resulting in $K\alpha$ abd $K\beta$ intensity ratios radically different from those obtained by light-ion excitation. An EDDT crystal was used for these measurements, giving better intrinsic energy resolution over the previous ADP crystal measurements. In addition, a 30.0-MeV oxygen-produced spectrum (not shown) with the ADP crystal showed the oxygen-produced $K\alpha$ diagram line to be only 10% broader than that from proton bombardment. Table II lists the experimental x-ray energies and energy shifts from the oxygen spectra along with calculated energies and initial configuration assignments which will be discussed later. In all oxygen-produced spectra the $K\alpha'$ transition was not observed, and only the KL and KL^2 satellite groups revealed multiplet structure. As listed in Table II and shown in Fig. 7, the energy shifts of the $K\alpha$ satellite lines varied little with the incident oxygen energy. In particular, both the most positive and most negative energy shifts from 13.0- and 35.0-MeV oxygen bombardment occurred for the KL^2 and KL^5 multiplets, respectively.

Figures 5 and 6 show striking differences in the $K\beta$ region of the Si and SiO_2 spectra as the oxygen energy is increased from 13.0 to 35.0 MeV. Overlapping $K\alpha$ satellite structure prevented observation of the $K\beta$ diagram band and the KL multiplet in the 13-MeV SiO_2 spectra. We note that the linewidths from SiO_2 are considerably larger than those from Si. The $K\beta$ energy shifts from the 13.0-MeV data are shown in Fig. 3 and are in general positive and decrease with increasing L-shell ionization, whereas for electron, proton, and helium bombardment, the $K\beta$ energy shifts are negative and increase with increasing L-shell ionization. No $K\beta$ energy shifts could be extracted

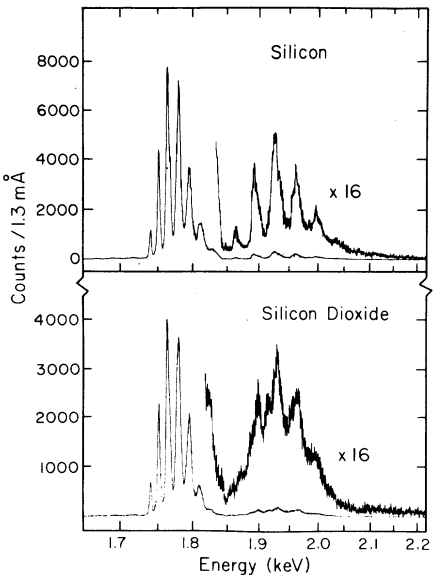

FIG. 5. Silicon and silicon dioxide K x-ray spectra produced from 13.0-MeV oxygen bombardment. The Si spectrum shows $K\alpha$ parent and satellite transitions with zero to six additional L-shell vacancies and $K\beta$ satellite transitions with one to six L-shell vacancies. The $K\beta$ parent band at 1.736 keV is not observed. The energies of the peak maxima are listed in Table II.

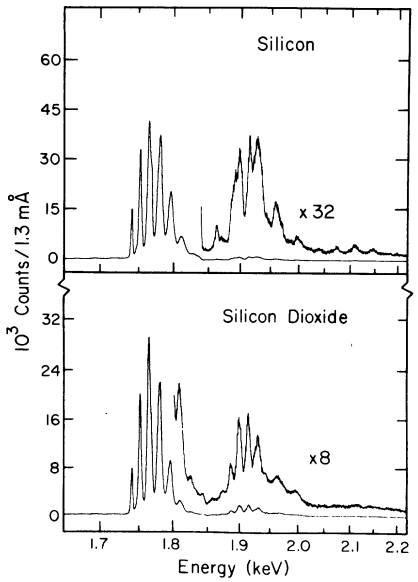

FIG. 6. Silicon and silicon dioxide K x-ray spectra produced from 35.0-MeV oxygen bombardment. The Si spectrum shows $K\alpha$ parent and satellite transitions with zero to six additional L-shell vacancies. The region from 1.85 to 2.05 contains both $K\beta$ satellite and $K\alpha$ hypersatellite transitions. The energies of the peak maxima are listed in Table II.

from the 35.0-MeV oxygen-produced spectra. At these high oxygen energies, the $K\alpha$ hypersatellite yields ($K\alpha$ satellite transitions with two inital K-shell vacancies) are large and obscure the $K\beta$ satellite yield. This problem will be discussed later.

In summary, our experimental results are the $K\alpha$ and $K\beta$, parent and satellite chemical energy shifts which have been extracted from the spectra. These results are listed in Tables I and II, and shown in Figs. 2 and 3. In particular, proton and helium bombardment give energy shifts similar to those produced by electron excitation. In addition, with helium bombardment we find that the $K\alpha$ energy shifts decrease with high L-shell ionization. The oxygen-produced spectra are dominated by the satellite structure, and similar to light-ion bombardment, the energy shifts for the $K\alpha$ satellite lines ranged from positive values to a pronounced negative value with increasing L-shell ionization. These shifts appear to be somewhat independent of the oxygen energy. Pronounced differences were found in the $K\beta$ satellite structure as the incident oxygen energy increased from 13.0 to 35.0 MeV. In the 13-MeV oxygen-produced spectra, large positive $K\beta$ shifts were observed which decreased with increasing L-shell ionization.

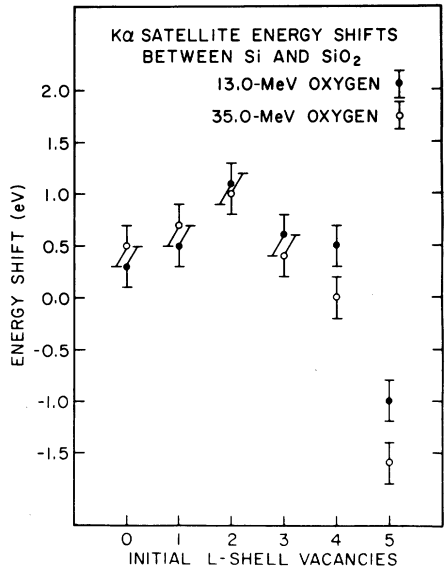

FIG. 7. Silicon $K\alpha$ parent and satellite chemical peak energy shifts between Si and SiO_2 observed with 13.0- and 35.0-MeV oxygen bombardment.

IV. DISCUSSION

A. Proton and helium bombardment

Chemical x-ray energy shifts are the result of changes in core binding energies, changes in multiplet structure, changes in valence-band energies, changes in the density of states in a valence band, and other effects. Current theoretical calculations which include these perturbations are very difficult, particularly for solids and x-ray transitions from valence bands. Hence, such calculations are limited to simple molecular systems which do not include silicon compounds, and so our experimental x-ray energies cannot be compared with detailed theoretical calculations. Nevertheless, some chemical effects can be estimated by free-ion models in which chemical bonding is simulated by adjusting the number of electrons in the valence shell in a free-atom calculation. To aid our qualitative understanding of these data, we have performed such calculations using the relativistic Hartree-Fock-Slater (HFS) computer code of Herman and Skillman[6] and the multiconfiguration Hartree-Fock (HF) computer code of Froese Fischer.[7] The x-ray transition energies were taken to be the difference in the calculated total binding energies before and after emission. Multiplet splittings were not considered. For silicon, HF and HFS calculations give similar energy shifts; those from HFS varied smoothly with L-shell ionization, whereas those from HF did not. Hence only shifts from HFS calculations are considered here. On the other hand, HF reproduced the absolute x-ray energies more accurately than HFS.

The $K\alpha$ chemical shifts measured from electron, proton, and helium bombardment are all similar as shown in Fig. 2. In particular, the shifts for the $K\alpha$ parent and first satellite multiplet from proton and helium bombardment are almost identical to those from electron bombardment. Moreover, the shifts for the KL^2 multiplet from proton and helium bombardment agree within experimental error. Positive shifts for the $K\alpha$ satellites occur, as discussed by Burkhalter *et al.*,[4] because the silicon atoms transfer M-shell electrons to their ligands during compound formation. This decreases the screening of inner-shell electrons resulting in tighter core binding energies for the molecules which give x rays of higher energies. We simulate this effect by performing HFS calculations for silicon x-ray satellite energies in which both one $3p$ electron and two $3p$ electrons are considered. If one $3p$ electron corresponds to SiO_2 and two $3p$ electrons correspond to Si, then the difference between the former and latter x-ray energies should be an estimate of the chemical effect for the satellite multiplets.

TABLE II. x-Ray energies and energy shifts from 13.0- and 35.0-MeV oxygen bombardment of Si and SiO_2.

Initial vacancies	x-Ray transition	x-Ray energy (eV) 13.0-MeV oxygen Si	13.0-MeV oxygen SiO_2	35-MeV oxygen Si	35-MeV oxygen SiO_2	HF	Energy shifts (eV) 13.0 MeV	35.0 MeV
K	$K\alpha_{1,2}$	1739.4	1739.7	1739.4	1739.9	1737.1	+0.3	+0.5
KL	$K\alpha_3$	1750.5	1751.0	1750.5	1751.2	1747.9	+0.5	+0.7
KL	$K\alpha_4$	•••	•••	1753.1	•••	1747.9	•••	•••
KL^2	$K\alpha_5$	1762.4	1763.5	1762.8	1763.8	1760.2	+1.1	+1.0
KL^2	$K\alpha_6$	1766.0	•••	1766.3	•••	1760.2	•••	•••
KL^3	$K\alpha$	1778.2	1778.8	1778.4	1778.8	1773.4	+0.6	+0.4
KL^4	$K\alpha$	1793.0	1793.5	1793.5	1793.5	1788.3	+0.5	0.0
KL^5	$K\alpha$	1809.1	1808.1	1808.8	1807.2	1805.3	−1.0	−1.6
K	$K\beta$	•••	•••	•••	•••	1838.2	•••	•••
KL	$K\beta''$	1862.4	•••	1863.0	•••	1870.1	•••	•••
KL	$K\beta'''$	•••	•••	1871.2	•••	1870.1	•••	•••
K^2	$K\alpha$	•••	•••	•••	1875.0	1875.6	•••	•••
K^2L	$K\alpha$	•••	•••	•••	1886.6	1887.9	•••	•••
KL^2	$K\beta$	1891.7	1900.1	1892.1	•••	1904.6	+8.4	•••
K^2L^2	$K\alpha$	•••	•••	1898.7	1899.9	1901.6	•••	•••
K^2L^3	$K\alpha$	•••	1915.1	1914.8	1914.5	1916.2	•••	•••
KL^3	$K\beta$	1925.7	1930.9	1926.0	•••	1941.4	+5.2	•••
K^2L^4	$K\alpha$	•••	•••	•••	1930.2	1932.4	•••	•••
KL^4	$K\beta$	1960.4	1965.4	1960.7	1966.3	1981.1	+5.0	+5.6
KL^5	$K\beta$	1996.3	1996.3	1997.4	•••	2023.2	0.0	•••

The results of these calculations are listed in the last column of Table I and plotted as a dashed line in Fig. 2. They show the $K\alpha$ shifts to be a monotonically increasing function of L-shell ionization, and moreover, they are in reasonable quantitative agreement with the experimental shifts, for the parent and first two satellite multiplets. However, for higher L-shell ionization the experimental shifts decrease with increasing ionization. This discrepancy will be discussed later.

The electron, proton, and helium-produced $K\beta$ shifts, shown in Fig. 3, are all negative and agree with each other within experimental error except for the $K\beta$ diagram shift from helium bombardment which is less negative. The additional third peak at 1874 eV observed in the KL multiplet of the SiO_2 spectra will not be considered here, but discussed later. The large negative shifts of the remaining transitions are mostly the result of a negative shift in the valence band of SiO_2 which according to Ershov and Lukirskii[8] is 5.8 eV more bound than that of Si. A free-ion model cannot simulate these negative shifts because solid-state effects are not incorporated; however, such calculations should be able to give the change in the energy shifts with L-shell ionization. HFS $K\beta$ shifts, analogous to the previous $K\alpha$ shifts, are listed in Table I and shown as a dashed line in Fig. 3. These shifts have been normalized by subtracting 8.4 eV from each HFS shift so as to negate the effect of the different valence-band energies and give the correct shift for the $K\beta$ diagram band. After this subtraction the resulting approximate shifts provide a reasonable reproduction of the light-ion data.

Both the energy and relative intensity of the $K\beta'$ transition located on the low-energy side of the diagram $K\beta$ band in the proton and helium-produced SiO_2 spectra were measured. This transition only occurs in compounds. O'Brien and Skinner[9] have labeled it as a "crossover transition" in which an electron in the $2s$ shell of oxygen descends to fill a $1s$ vacancy in silicon. Assuming such a transition, we estimate its energy by taking the difference between the sums of the separate HF total energies for oxygen and silicon with the appropriate configurations. That is, configurations of $1s^22s^22p^4$ and $1s^12s^22p^63s^23p^2$ for oxygen and silicon, respectively, in the initial state and $2s^21s^12p^4$ and $1s^22s^22p^63s^23p^2$ in the final state. This gives a transition energy of 1813 eV which is in reasonable agreement with the experimental value of 1818 eV. However, as pointed out by Urch,[10] the crossover model provides a successful qualitative explanation, but ignores the reality of chemical bond formation. With a molecular-orbital group-theory approach Urch[10] predicted the intensity ratio of the $K\beta'$ band to the diagram $K\beta$ band to be roughly 0.25 to 0.30 for SiO_2, whereas we obtain 0.21 experimentally for this ratio.

B. Oxygen bombardment

The 13.0- and 35.0-MeV oxygen-produced spectra are completely unlike those produced by hydrogen and helium bombardment. Recoil effects from heavy-ion bombardment, which have been discussed in some detail by Burkhalter *et al.*,[4] do not appear to be significant in the present work. In Ref. 4, the width of the aluminum $K\alpha$ diagram line increased from 1.8 eV for helium bombardment to 3.1 eV for neon bombardment. This effect is less severe in the present work where oxygen bombardment increases the width of the silicon $K\alpha$ diagram line by only 10%. In addition, this line broadening does not appear to depend strongly on the incident oxygen energy.

Moreover, the $K\alpha$ energy shifts do not depend strongly on the incident oxygen energy. This is illustrated in Fig. 7 where the $K\alpha$ energy shifts from the two oxygen bombarding energies are shown. The 13.0-MeV shifts are also plotted in Fig. 2 which shows that these shifts follow the same general trend as those produced from light-ion bombardment. That is, for low ionization the energy shifts increase with increasing L-shell ionization as expected from free-ion calculations; however, for high-ionization states they unexpectly start to decrease. In fact, with oxygen bombardment a pronounced negative shift of -1.6 eV is measured for the KL^5 multiplet. This decrease in the chemical shifts cannot be understood with a free-ion model. We speculate that with increasing L-shell ionization, the effective charge for the outer shells increases and tends to attract the electron clouds of the neighboring atoms into the valence shells of silicon. Increasingly with L-shell ionization, this negates the loss of electron density in the valence shell owing to chemical bonding and crystal formation which results in smaller x-ray energies for the $K\alpha$ satellite multiplets. This in itself does not explain the energy shifts because if oxygen can provide electrons for screening in SiO_2, then neighboring Si atoms can provide electrons for a highly ionized Si atom. In fact, electrons are more mobile in Si than in SiO_2. However, the physical situation with these very high-charge centers is not understood. The experimental data indicates with increasing L-shell ionization that the screening for SiO_2 at the time of emission is more complete than that for Si which results in decreasing energy shifts. For the highly ionized state giving rise to the KL^5 multiplet, this difference in screening is so large that the oxygen appears to provide a net increase in electron density in the valence shells resulting in a negative energy shift. This effect can be simulated with a free-ion calculation. A negative energy shift of -2.4 eV is obtained for the KL^5 multiplet when SiO_2 and Si are allowed to have three $2p$ electrons and two $2p$ electrons, respectively.

The oxygen-produced x-ray structure observed in the $K\beta$ satellite region of the spectra shows striking differences between Si and SiO_2 targets and high and low beam energies. In particular, the 35.0-MeV spectrum has considerably more structure than the 13.0-MeV spectrum. This additional structure is due to $K\alpha$ hypersatellite transitions which overlap the usual $K\beta$ satellite transitions on the 35.0-MeV spectrum. Simple formalisms for multiple Coulomb ionization indicate that over this oxygen energy range the $K\alpha$ hypersatellite x-ray intensities would increase much faster with beam energy than the $K\beta$ satellite intensities. This expected behavior has been verified to some extent by measurements of 24.0–48.0-MeV oxygen bombardment of calcium where the relative intensity of double K-shell ionization with respect to single K-shell ionization increases by an order of magnitude.[11] Moreover, HF calculations predict that $K\alpha$ hypersatellite and $K\beta$ satellite x-ray energies will overlap for silicon.

The results of such calculations are compared with the experimental energies from oxygen bombardment in Table II. Ignoring the very small chemical shifts, the top half of Table II shows that the calculated $K\alpha$ satellite energies (column 7) are in good agreement with the experimental values. In particular, all the $K\alpha$ satellites energies are reproduced to within 5.5 eV, and the relative energies are predicted considerably better. The bottom half of Table II gives a comparison with the $K\beta$ satellite and $K\alpha$ hypersatellite energies which helps to identify these transitions. In particular, all five broad peaks observed in the 13.0-MeV oxygen-produced Si spectrum are $K\beta$ satellite transitions. The agreement with the HF results is not as good, but the general trend of the data is reproduced. This is perhaps not too surprising because the $K\beta$ transitions involve the valence band and hence depend strongly on the chemical environment, whereas the $K\alpha$ transitions depend only on the inner shells were the chemical effects provide only a small perturbation.

The 35.0-MeV oxygen-produced radiation in the $K\beta$ region is much more complicated. With the aid of HF calculations and the 13.0-MeV spectra, we have identified the major configuration of some of the hypersatellite transitions as shown in Table II, where only experimental transitions with well-defined peaks are listed. The narrow peaks which are particularly pronounced on the SiO_2 spectra are all $K\alpha$ hypersatellite multiplets.

The HF calculated energies for these multiplets are in good agreement with the experimental values. The broader peaks are $K\beta$ satellite transitions whose experimental energies are all within 1.1 eV of the 13.0-MeV $K\beta$ satellite energies. The 1915-eV line on the 13.0-MeV oxygen-produced SiO_2 spectrum is sharp and has the correct energy to be the K^2L^3 hypersatellite multiplet. Perhaps this indicates that part of the 13.0-MeV oxygen-produced $K\beta$ radiation is in fact from $K\alpha$ hypersatellite transitions. Nevertheless a comparison of the 13.0- and 35.0-MeV spectra indicates that most of the 13.0-MeV oxygen produced radiation in this region is from $K\beta$ transitions.

The chemical shifts for these 13.0-MeV oxygen-produced $K\beta$ transitions are also shown in Fig. 2. Similar to Burkhalter *et al.*[4] we measure some of the satellite $K\beta$ chemical shifts from heavy-ion bombardment to be very large. In particular, for the KL^2 multiplet we obtain a shift of +8.4 eV from oxygen bombardment and −1.6 eV from helium bombardment. This anomaly could be caused by x-ray transitions from the conduction band in SiO_2.[12] Reilly[13] calculates with molecular-orbital theory that the conduction band of SiO_2 is 8.5 eV higher in energy than its valence band. Ershov and Lukirskii[8] measured this gap to be around 7.0 eV, whereas DiStefano and Eastman[14] measured the gap to be 9.0 eV. Hence, if heavy-ion bombardment excited electrons up to the conduction band in SiO_2 or populated the conduction band directly, while simultaneously ionizing the K and L shells of Si, apparent chemical shifts of the order of 10.0 eV would issue with the resulting deexcitation X rays. In other words, the large chemical shifts from oxygen bombardment are the result of transitions from the conduction band in SiO_2 and transitions from the valence or conduction band in Si. Because Si is a semiconductor, its valence and conduction band are very close in energy. A similar effect has been reported by Fortner, Der, and Kavanagh[15] for projectile x rays from normally empty core levels in Xe.

The absolute x-ray energies of these lines are consistent with this hypothesis. Helium and oxygen bombardment give 1892.4 and 1891.7 eV, respectively, for the Si target and 1890.8 and 1900.1 eV for the SiO_2. Thus the 8.4-eV chemical shift results mostly from a 9.3-eV increase in energy for the SiO_2 KL^2 multiplet with oxygen bombardment. In addition to transitions from the excited band we would expect to observe transitions from the valence band. The 13.0-MeV $K\beta$ satellite lines are wider and reveal shoulders with respect to the corresponding lines on the Si spectrum, which could be the valence-band transitions. However, as discussed previously this additional radiation could also be from hypersatellite transitions or other effects.

In addition, the third transition of the KL multiplet at 1874 eV observed in hydrogen and helium bombardment probably arises from a higher band. If we consider this transition in SiO_2 to correspond to the second peak of this multiplet in Si we would obtain chemical shifts of 5.1 and 4.8 eV from hydrogen and helium bombardment, respectively, which has the magnitude of the oxygen-produced shift. The decrease in the $K\beta$ shifts with high L-shell ionization could again result from a more effective screening of the high-charge centers by neighboring oxygen atoms than by neighboring silicon atoms.

In summary, this work verifies some of the earlier quantitative findings of Burkhalter *et al.*[4] for x-ray chemical shifts produced from light-ion and heavy-ion bombardment of solids. Moreover, our spectra indicate that perhaps the anomalously large positive, heavy-ion produced, $K\beta$ chemical shifts are due to transitions from higher bands in these solids which normally are empty. Both $K\alpha$ and $K\beta$ chemical shifts for high L-shell ionization have been measured to decrease with increasing L-shell ionization. Further experimental and theoretical work is required to obtain a better understanding of chemical shifts from highly ionized compounds.

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