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Chemical Effects on Ion-Excited Aluminum *K* X-Ray Spectra

P. G. Burkhalter, A. R. Knudson, D. J. Nagel, and K. L. Dunning
Naval Research Laboratory, Washington, D. C. 20390

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Five-MeV He and Ne ions were used to excite the aluminum $K\alpha$ and $K\beta$ parent and satellite x-ray spectra of Al metal, oxide, and nitride. Compared to the metal, the $K\alpha$ line and $K\alpha$ satellites from the oxide were at energies a few tenths of an eV higher with helium-ion excitation, similar to observations with electron excitation. With neon bombardment, the $K\alpha$ satellite lines were broader and the energy shifts reduced because of target-atom recoil effects. The chemical shifts in the $K\beta$ spectra vary from negative in the parent band with helium ions to positive shifts as large as 6 eV in the higher-energy $K\beta$ satellites produced by neon ions, and were found to depend on the degree of L-shell ionization.

INTRODUCTION

X-ray spectra are sensitive to the chemical environment of the emitting atom and can yield information on the atomic and electronic structure of materials.[1] Chemical shifts, defined as the peak x-ray energy from a compound minus that from the metal, have previously been measured for $K\alpha$ and $K\beta$ spectra in Al compounds with photon and electron excitation.[2–9] The present study follows from earlier observations that both light[10] and heavy[11] ions are effective in producing multiple inner-shell ionization in aluminum metal. X-ray satellites, occurring at energies higher than the normal x-ray parent lines, result from multiple ionization.[12] Because of enhanced satellite intensities with ion excitation, higher-energy x-ray satellites can be measured using ion rather than electron bombardment. This work, which is the first study of chemical effects on ion-excited x-ray spectra, was done to search for new effects of possible use for the study of materials.

Energy shifts were measured in the $K\alpha$ and $K\beta$ parent line and satellite spectra of aluminum metal and its compounds; both helium- and neon-ion excitation were employed. This selection allows study of chemical combination effects on both inner-shell transitions, Al $K\alpha$, and valence-band spectra, Al $K\beta$, with incident particles of widely different mass. Our major findings are that chemical shifts for the $K\alpha$ line and $K\alpha$ satellites with helium-ion excitation are similar to those with electron excitation, but recoil effects appear in neon-excited $K\alpha$ spectra. Positive energy shifts for higher-energy $K\beta$ satellites in the oxide and nitride spectra are found for the first time.

EXPERIMENTAL CONDITIONS AND DATA HANDLING

The 5-MV Naval Research Laboratory Van de Graaff produced ^{4}He and ^{20}Ne beams. Beam currents were typically 0.3 μA. Samples were positioned at 45° to the ion beam and the x rays emitted by the targets at 90° to the beam direction passed through an entrance collimator to a computer-controlled step-scanning Bragg spectrometer employing flat-crystal x-ray optics. For collecting $K\alpha$ spectra an EDDT crystal ($2d$ spacing $= 8.808$ Å) was used. The entrance collimator was a fine-blade commercial x-ray collimator, 10.2 cm long, which provided collimation of 0.07°. A short coarse 0.8° collimator placed in front of the detector was effective in improving the peak-to-background ratio. For the weaker $K\beta$ spectra, data were collected with a coarser entrance collimator 1.9 cm long with 0.038-mm blade spacing and without the detector collimator. Intensity was also increased by using a PET crystal ($2d$ spacing $= 8.742$ Å). Because PET has a large thermal coefficient of expansion, the spectrometer was brought to thermal equilibrium before taking data. A P-10 gas-flow proportional detector with a grid-supported stretched-polypropylene detector window was used.

Thick samples of Al metal, Al_2O_3, and AlN were used for the measurements. In order to prevent charging, the oxide and nitride samples were coated with 250 Å of gold (which corresponds to a 100-keV energy loss for 5.0-MeV neon ions). Without a conducting coating, charging results in a superposition of electron plus ion-excited spectra due to breakdown between the target holder and the oxide target. This effect was previously reported by Terasawa.[13]

Since the primary purpose of this work was to measure spectral shifts, and since energy shifts could be accurately obtained from relative intensities, the data have not been corrected for crystal and detector efficiency or for self-absorption in the samples. Published values of the $K\alpha_{1,2}$ and $K\beta$ energies were used to establish the energy scale of the spectrometer from proton-excited aluminum spectra. Energies of the x-ray peaks were obtained by least-squares computer unfolding into Gaussian components.

RESULTS

In this section we will first examine the $K\alpha$ and $K\beta$ spectra excited by helium and then the same spectra produced by neon impact. Figure 1 shows the helium-excited $K\alpha$ spectra from Al metal and oxide. We find that the satellite intensities are enhanced with respect to electron excitation for the oxide as well as for the metal. The first large $K\alpha$ satellite group, consisting of the $\alpha_3\alpha_4$ satellites, occurs because of a single L-shell vacancy existing during the inner-level $2p \rightarrow 1s$ transition. In electron or photon excitation, the α_3, α_4 satellites result from electron shakeoff and are only 10% of the intensity of the parent line,[14] whereas with helium excitation, the $\alpha_3\alpha_4$ grouping is 75% or more of the integrated intensity of the parent line and can be explained by multiple Coulomb ionization.[10] Except for the oxide α_4/α_3 ratio, which is less than that observed with electron excitation, the shapes of the satellite spectra shown in Fig. 1 are similar to previous observations. In Table I are listed the $K\alpha$ line and satellite energies for metal and oxide produced with helium-ion bombardment. The peak shifts have an estimated precision of ± 0.1 eV. The $K\alpha_{1,2}$, α', α_3, and α_4 peak shifts are seen to be in better agreement with energy shifts using electron excitation reported by Baun and Fischer[2] and Nordfors[3] than with those of Demekhin and Sachenko.[4] The α_5 and α_6 peak shifts are smaller than Baun and Fischer's values.

Figure 2 shows the $K\beta$ spectra excited by helium ions for Al metal and oxide. Electron-excited spectra showing the $K\beta'$ transition in the oxide spectrum and the $K\beta_1$ band for metal and oxide are included in this figure. The negative 3.4-eV peak shift for the $K\beta_1$ parent band in Al_2O_3 obtained with light-ion excitation is due mainly to direct bonding effects on the valence electrons and corresponds to the large negative shift found with electron excitation. Energy shift values for the $K\beta_1$ band measured at the maximum intensity of the peak range from -4.4 to -5.4 eV.[3,6,7]

The two $K\beta$ satellite groupings are the $K\beta^{III}\beta^{IV}$ and $K\beta^{VII}\beta^{VIII}$ bands which correspond to one and two L-shell vacancies during the $3p \rightarrow 1s$ transition. Karlsson and Siegbahn[5] measured Al metal and oxide spectra photographically. The faint $K\beta^{III}\beta^{IV}$ satellite peaks on their plots show negative shifts but a quantitative measurement was not reported. Fischer and Baun[6] measured peak shifts of -3.9 eV for $K\beta^{III}$ and -3.2 eV for $K\beta^{IV}$ satellites, which are smaller shifts than their -4.4 eV for the $K\beta_1$ parent band. Peak-shift data were not found in the literature for the higher-energy $K\beta^{VII}\beta^{VIII}$ satellites. Table II lists the energies and peak shifts for the $K\beta$ satellites produced with helium excitation. The peak shifts are believed accurate to ± 0.3 eV. Variation in the $K\beta$ peak shifts from negative to positive as the degree of ionization increases will be discussed later.

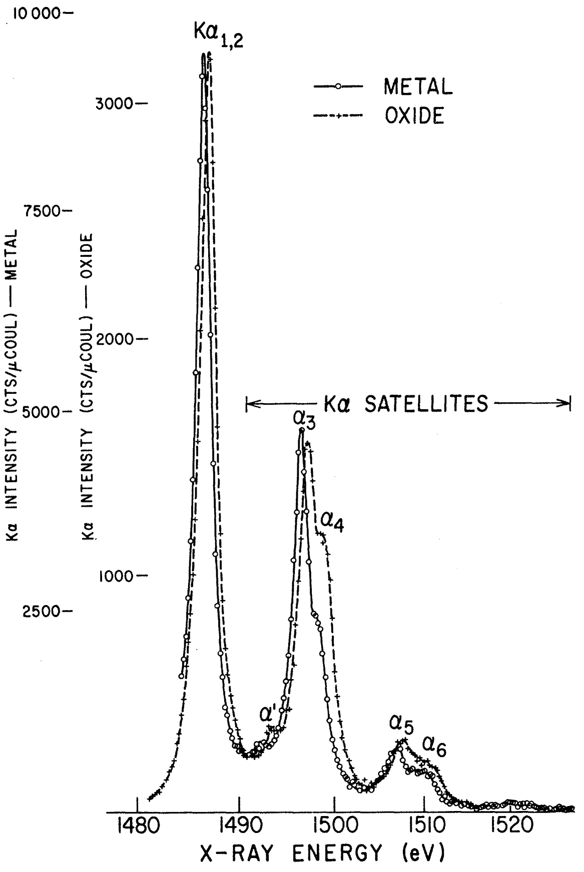

FIG. 1. $K\alpha$ spectra for Al metal and oxide excited with 5.0-MeV ^4He ions. Each point in the metal spectrum was collected for 1.0 μC while 2.0 μC was used as preset charge in the oxide spectrum.

The neon-excited $K\alpha$ spectra for Al metal and oxide are shown in Fig. 3. Each successive satellite group corresponds to an additional L-shell vacancy, besides the initial K-shell vacancy, as previously identified in the Al metal spectra with nitrogen ions.[11] Over all, the metal and oxide spectra due to neon impact are strikingly similar. The spectral details of multiplet splitting are less distinct in the neon spectra than in the helium spectra. In particular, no $\alpha_3\alpha_4$ structure is observed, but multiplet splitting still remains in both oxide and metal spectra for the two most intense satellites. The spectral details of multiplet splitting are less distinct in the heavy-ion excited spectra because of Al–target-ion recoil effects, including Doppler broadening, which will also be discussed later. Small positive peak shifts are discernible which increase from less than 0.1 eV for the parent line to the largest shift of 0.4 eV in the

TABLE I. Peak energies and chemical shifts in eV for $K\alpha$ spectra excited by helium ions and chemical shifts obtained by electron excitation.

X-ray peak	Vacancy configuration	X-ray energy Metal	Oxide	Energy shifts Present work $^4He^+$	Baun-Fischer[a] e^-	Nordfors[b] e^-	Demekhin-Sachenko[c] e^-	ΔE_{SCF} calc.
line $\alpha_{1,2}$	K	1486.6	1487.0	+0.4	+0.3	+0.3	+0.5	+0.5
sat. α'	KL^1	1492.8	1493.8	+1.0	+0.7		+0.85	+0.7
sat. α_3	KL^1	1496.4	1497.1	+0.7	+0.6	+0.6	+0.9	+0.7
sat. α_4	KL^1	1498.6	1499.2	+0.6	+0.6	+0.6	+0.9	+0.7
sat. α_5	KL^2	1506.8	1507.3	+0.5	+0.9			+1.0
sat. α_6	KL^2	1510.2	1510.7	+0.5	+0.9			+1.0

[a] Reference 2. [b] Reference 3. [c] Reference 4.

third satellite group.

The $K\beta$ satellites produced by neon ions are shown in Fig. 4 for metal and oxide. The counting statistics were poor for the weaker satellite lines, particularly in the oxide spectra, and only shifts in the larger peaks could be identified. As in Fig. 2, the $K\beta'$ bands fill in valleys between peaks of the oxide spectra. The bump in the neon-excited spectra at about 1600 eV is believed to be the β' band corresponding to the 1614.7-eV satellite. Unexpectedly, the $K\beta$ satellites corresponding to two or more L-shell vacancies had large positive energy shifts which depend on the number of L-shell vacancies. To give further experimental support to these findings the $K\beta$ spectrum for AlN was measured and peak energies and shifts are tabulated in Table III. The $K\beta$ satellite peaks are more distinct in the neon-produced AlN spectra because the β' transitions are less intense than in the oxide spectra. The peak shifts for the nitride are less than for the oxide as shown in Table III. For both oxide and nitride the shifts became smaller as the number of L-shell vacancies increase. The shifts were obtained at the peak maximum

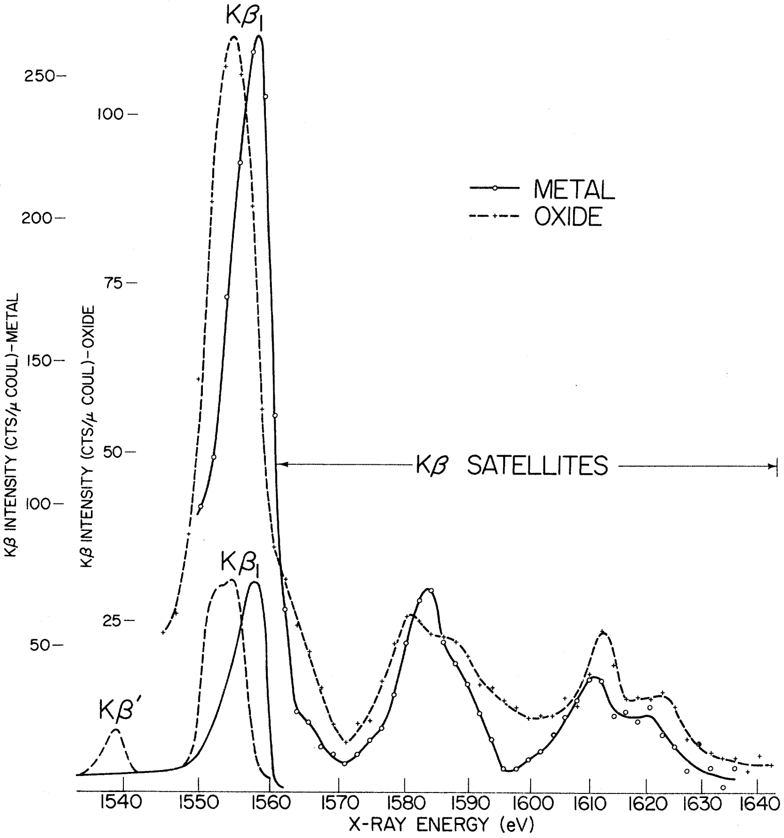

FIG. 2. $K\beta$ spectra for Al metal and oxide excited with 5.0-MeV helium ions with 10- and 80-μC charge collections, respectively, together with electron-excited data of Dodd and Glen (Ref. 15) showing the $K\beta'$ and $K\beta$ bands in Al metal and oxide.

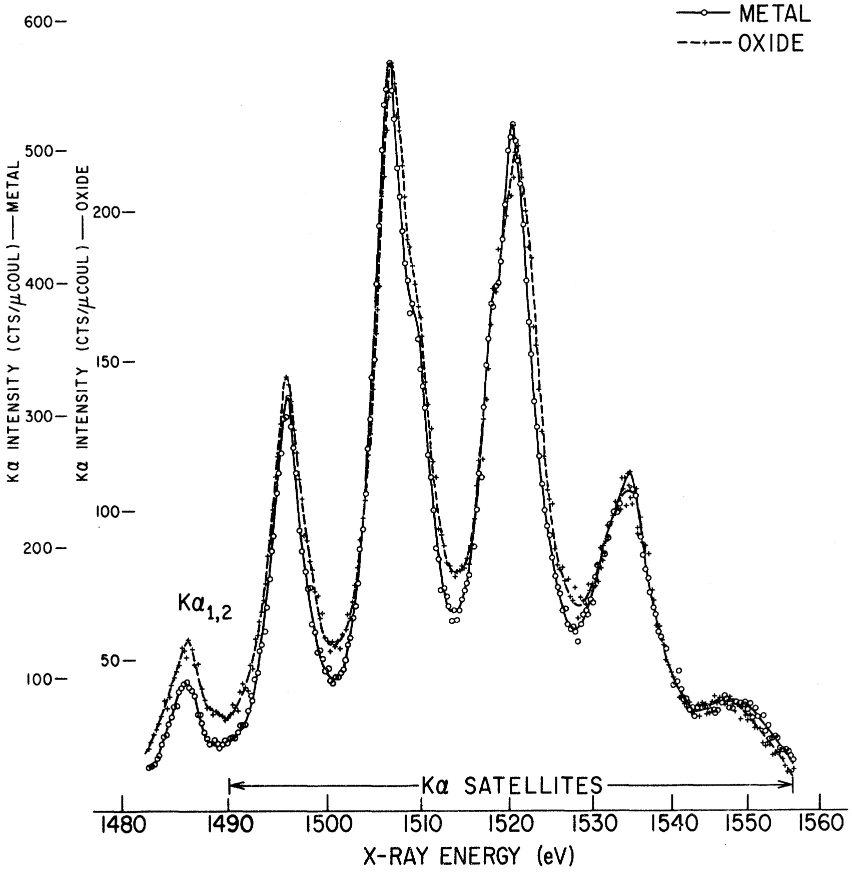

FIG. 3. $K\alpha$ spectra for 5.0-MeV ^{20}Ne-ion bombardment of Al metal and oxide with 10- and 15-μC charge collections, respectively.

with an estimated accuracy of ±0.5 eV for the more intense peaks. The $K\beta_1$ band cannot be measured in the heavy-ion spectra because of overlap by the intense $K\alpha$ satellite corresponding to five L-shell vacancies.

Summarizing our experimental results, we find that the light-ion–excited spectra show similarities with photon and electron spectra, particularly in the $K\alpha$ spectra where the few tenths eV shifts agree with published electron-excitation data. We obtained a negative shift of several eV in the $K\beta_1$ parent band with helium ions as with electron-produced spectra, but the energy shift in the $K\beta$ satellites changes from negative to positive with increasing L-shell ionization. The heavy-ion–excited spectra are dominated by satellite production and therefore are quite different from electron or light-ion spectra. The most prominent features are large positive peak shifts in the $K\beta$ satellites which decrease with increasing L-shell ionization.

DISCUSSION

A number of effects can cause chemical shifts in x-ray spectra, such as changes in core-level binding energies and valence-level energy shifts, changes in the density of states, and changes in multiplet structure. Procedures for calculating x-ray spectral shifts in solids are complex because of the above-mentioned effects, particularly in situations where x rays arise from valence

TABLE II. Peak energies and chemical shifts in eV for $K\beta$ spectra excited by helium ions and electrons.

X-ray peak	Vacancy configuration	Energy metal	Energy oxide	Energy shift	Fischer–Baun[a] e^-
$K\beta_1$ line	K	1557.5	1554.1	−3.4	−4.4
$K\beta^{\mathrm{III}}$ sat.	KL^1	1582.3	1580.6	−1.7	−3.9
$K\beta^{\mathrm{IV}}$ sat.	KL^1	1589.2	1588.6	−0.6	−3.2
$K\beta^{\mathrm{VII}}$ sat.	KL^2	1610.0	1611.4	+1.4	
$K\beta^{\mathrm{VIII}}$ sat.	KL^2	1620.3	1623.4	+3.1	

[a] Reference 2.

TABLE III. Peak energies and chemical shifts in eV for $K\beta$ satellites excited by neon ions.

X-ray satellite group	Vacancy configuration	Energy metal	Energy oxide	Metal-oxide shift	Energy nitride	Metal-nitride shift
1st	KL^1	1580.7				
2nd	KL^2	1608.2	1614.7	+6.3	1611.5	+3.3
3rd	KL^3	1638.3	1643.5	+5.2	1641.5	+3.2
4th	KL^4	1670.7	1673.9	+3.2	1672.0	+1.3
5th	KL^5	1702.1				

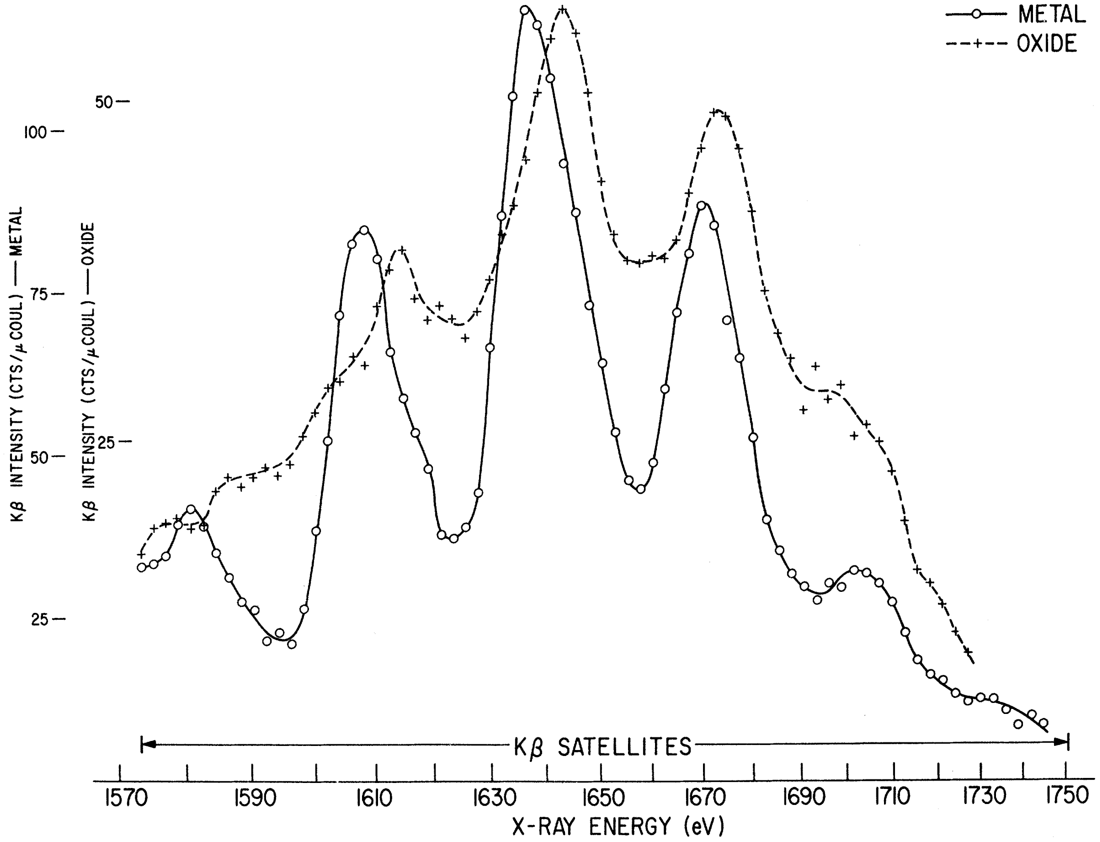

FIG. 4. *Kβ* satellite spectra for 5.0-MeV Ne-ion bombardment of Al metal and oxide with 20- and 45-μC charge collections, respectively.

bands in compounds. X-ray energy calculations using free-ion models have been valuable in identifying both core- and valence-level x-ray satellite energies in Al metal.[11] In this work we have applied the free-ion model to both the metal and a simulated electronic configuration for Al oxide and tried to correlate calculated shifts with our experimental results. X-ray energy calculations with Hartree–Fock–Slater wave functions have been made by taking differences in the self-consistent field calculations (ΔE_{SCF}) of the total initial and final binding energies for the atomic configurations resulting in $K\alpha$ and $K\beta$ x-ray transition for various degrees of multiple ionization.

Light-Ion Excitation

The chemical shifts in our light-ion induced spectra will be discussed by comparing them with spectra from electron excitation and with theoretical calculations. Positive energy shifts in both $K\alpha$ lines and satellites in x-ray spectra for Al metal and oxide result from increased inner-shell binding energies due to transfer of M-shell electron to oxygen atoms during compound formation. As shown in Table I, it was observed with electron excitation that the positive $K\alpha$ chemical shift increased with the degree of L-shell ionization. Demekhin and Sachenko[16] showed that such an increase should be expected from changes in screening constants. We performed ΔE_{SCF} calculations assuming that the 3s electrons of the Al atom are responsible for compound formation, that is, $K\alpha$ x-ray energies were computed for various degrees of L-shell ionization with a $(3s)^2(3p)^1$ configuration for Al metal and with a $(3s)^1(3p)^1$ configuration to simulate an Al ion in the oxide. The ΔE_{SCF} calculations gave positive energy shifts of 0.5, 0.7, and 1.0 eV for the $K\alpha_{1,2}$ line, one L-shell vacancy (α', α_3, α_4), and a double L-shell vacancy satellite (α_5, α_6), respectively, as listed in Table I. The data of Baun and Fischer show an increase in positive energy shift per degree of L-shell ionization consistent with our ΔE_{SCF} calculations. Our helium data have an unexplained small energy shift for the α_5 and α_6 satellites.

The large negative energy shift of the parent $K\beta_1$ band in going from metal to oxide is the net result of negative shifts of the entire valence band

and of the peak in the density of states within the band, plus a smaller positive K-level shift. The Al metal and oxide atomic level diagrams have been worked out by Fomichev[17] from x-ray emission and absorption data. The top of the valence band in Al_2O_3 is 5.3 eV lower than in the metal. We know from the $K\beta_1$ band shapes that the electron distribution is more symmetric in the oxide than in Al metal, as can be seen in both the electron and the helium data in Fig. 2. The actual energy shift measured between peak maxima ranges from -4.4 to -5.4 eV for electron excitation. With helium ions a less negative -3.4-eV shift was observed. This value was experimentally reproducible and may indicate a difference between light-ion and electron excitations.

The free-ion-model calculations predict a chemical shift of $+4.6$ eV for the $K\beta_1$ parent line in contrast to the negative shifts that occur in light-ion and electron data. Because of free-ion model neglects the major solid-state effects in valence x-ray spectra it has limited utility in predicting absolute $K\beta$ chemical shifts, but it is still useful for calculating changes in $K\beta$ energies as a function of L-shell ionization.

A major difference between helium and electron excitation is that the satellite energy shifts tend towards positive energies with a larger slope for ions than for electrons, as can be seen in Fig. 5, where $K\beta$ energy shifts for various projectiles and compounds are plotted as a function of the degree of L-shell vacancy. The change in the $K\beta$ chemical shift per unit of L-shell ionization is about $+2.3$ eV for helium ions but only $+0.7$ eV from the $K\beta_1$ band to the center of gravity of the $\beta^{III}\beta^{IV}$ satellite measured by Fischer and Baun. The ΔE_{SCF} calculations yielded a change in the $K\beta$ chemical shift per degree of L-shell vacancy of $+0.7$ eV, in agreement with the limited electron data, even though direct bonding effects are not properly taken into account. The more positive slope of 2.3 eV for helium ions suggests further alteration of the M-shell occupancy. However, a slope that large is not predicted even with an oxide simulated by an empty M shell. Because the mobile conduction electrons would be attracted to and would screen a highly charged ion in the metal, the slope of the $K\beta$ shift could be calculated by adding M-shell electrons to the metal. But to do this would introduce inconsistencies in the $K\alpha$ energy shifts.

Heavy-Ion Excitation

The chemical shifts measured in the light-ion $K\alpha$ spectra are not as apparent in the neon-produced $K\alpha$ spectra, and spectral broadening has obscured much of the multiplet structure. We have found large positive chemical shifts in the neon-excited $K\beta$ spectrum in high-energy satellites that are not measurable in electron-excited data and which are not explainable with free-ion calculations. Hence both the $K\alpha$ and $K\beta$ spectra indicate that other physical phenomena need consideration for x-ray spectra produced by massive high-energy projectiles. Direct influence of the electronic structure of the projectile during x-ray emission can be eliminated because a 5-MeV neon ion can travel about 50 lattice spacings during the K-shell hole lifetime of 2×10^{-15} sec given by McGuire.[18] Therefore the neon ion has left the vicinity of the excited target atom before the K-vacancy decays.

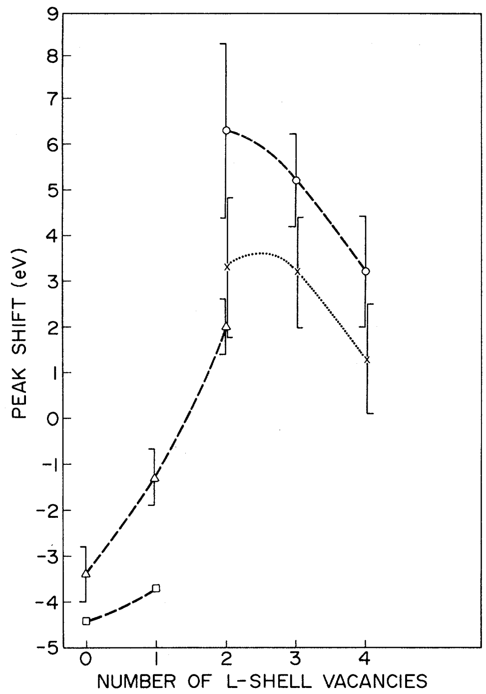

FIG. 5. Peak shifts for Al $K\beta$ spectra of metal (M), oxide (O), and nitride (N) vs number of L-shell vacancies. ○, Ne^+ (O-M); ×, Ne^+ (N-M); Δ, He^+ (O-M); □, e^- (O-M).

The use of heavy projectile ions such as neon, whose nuclear charge is five times that of the helium nucleus and whose mass is comparable to that of the aluminum target atoms, makes highly probable the transfer of sufficient energy to the recoiling target atoms to produce observable Doppler broadening of the emitted x rays and other effects caused by the ejection of the emitting Al ion from its lattice site. A classical picture of the collision was used to calculate the velocity distribution of the recoiling aluminum atoms whose K shell had been excited by the neon projectile. The tables of Bingham[19] were used to obtain the scattering angle of the incident neon ion as a function of impact parameter for a screened Coulomb interaction between the Ne and Al atoms. For a given impact parameter, the velocity of the Al ion after the collision was calculated and the probability of exciting a *K*-shell electron was obtained using the calculated values of Hansteen and Mosebekk[20] for 0.2-MeV protons on aluminum, since these were the most suitable data available in the literature. Protons of this energy would have the same velocity relative to the Al atoms as 4.0-MeV neon ions. The calculated velocity distribution of the recoiling aluminum ions with *K*-shell vacancies peaked at 3.5×10^6 cm/sec, which was an order of magnitude larger than the corresponding value for helium projectiles.

The computed velocity distribution was first applied to calculate Doppler broadening. Collisions, for which the distance of closest approach between the Ne and Al ions is of the order of the Al *K*-shell radius, result in projectile deflections of a few degrees, but produce Al target ions recoiling at about 90° to the beam, which corresponds to our detection angle. Calculations yielded a full width at half-maximum (FWHM) due to Doppler broadening of about 0.6 eV. This is considered to be a rough estimate and indicates that Doppler broadening should be detectable in high-resolution x-ray spectra excited by heavy ions, if it is not overwhelmed by broadening due to other effects. This estimate would have to be four times larger to account for the observed broadening of the $K\alpha_{1,2}$ line from 1.8 to 3.1 eV in going from helium to neon excitation. Similarly, a factor of 4 would also account, to within 10%, for the increased widths of the first three $K\alpha$ satellites in the neon-excited spectra. It is believed that the Doppler-broadening calculations are reliable to better than a factor of 4 and therefore the observed increase in linewidth in going from He to Ne excitation does not appear to be explainable by Doppler broadening alone. Furthermore, the neon-excited $K\beta$ bands appear to exhibit an additional broadening of the order of 6–8 eV in comparison to the broadening in the helium-excited $K\beta$ bands. This is an order of magnitude greater than our prediction for the Doppler broadening.

The lack of agreement between observed and computed broadening requires examination of other effects following from Al-ion recoil. The calculated velocity distribution indicates that 60% of the recoiling Al ions with *K*-shell vacancies have a velocity sufficient to travel at least 1 Å in the lifetime of the *K*-shell vacancy (2×10^{-15} sec) and about 45% travel 1 Å in the half-life of the *K*-shell hole. This displacement of the emitting Al ion from its lattice site could produce changes in the x-ray energy due to spatial variations in the electron density and crystal field. That is, recoil will cause changes in the molecular orbitals normally present. Also, impact of the recoiling ions on neighboring atoms may produce *M*-shell vacancies in addition to any produced in the initial projectile-target encounter. These mechanisms would be expected to have a greater influence on the *M* shell than on the *K* and *L* shells, since the *M* shell is more loosely bound and of greater spatial extent. Thus, these recoil effects should appear more prominently in the $K\beta$ spectrum, which is in accord with the great increase in width observed for the $K\beta$ bands in going from He to Ne excitation.

It can be noted that, although the helium-excited Al $K\alpha_{1,2}$ line in the present work has a linewidth of 1.8 eV compared to 2.5 eV for the proton-excited Si $K\alpha_{1,2}$ line in the work of McGrary and Richard,[21] we are not able to see the multiplets in the neon-excited $K\alpha$ spectrum that appear in their 30-MeV oxygen-excited Si $K\alpha$ spectrum. This may be at least partially explained because the recoil energy is about an order of magnitude less in their experiment, thus reducing the relative importance of recoil effects.

We have examined the various possible recoil effects and available interpretations of valence-band x-ray energies to search for an explanation of the large positive $K\beta$ shifts in our neon data. Urch[22] has used molecular-orbital theory (MO) to calculate the electronic bonding structure in alumina. He interpreted chemical shifts in the $K\beta'$ and $K\beta_1$ bands by use of MO levels. Reilly[23] has calculated the valence bands in Al_2O_3 using MO theory and finds an unfilled level associated only with bonding between Al ions, about 9 eV above the filled band, in agreement with an experimentally measured exciton of 9.5 eV for Al_2O_3. The experimental gap of 6.3 eV between the conduction band and the filled band presented by Fomichev[17] for Al_2O_3 is consistent with the MO model. Thus the concept that an ion-atom collision energy in excess of inner-shell ionization could excite electrons to unfilled levels and produce positive peak shifts of 6 eV or larger is a plausible hypothesis; however, this hypothesis can be ruled out as an explanation for the $K\beta$ satellite shifts in the neon-excited data because the unfilled band in the compound should result in higher absolute x-ray energies for the oxide data in contrast to our experimental observations. The absolute x-ray energy for the second $K\beta$ satellite group in the oxide spectra does not change in going from helium to neon excitation. The difference in chemical shift in the helium- and neon-produced spectra results from a shift in the absolute $K\beta$ energy for the metal, which is 5 eV less in the second satellite group and 4 eV less in the first satellite group, with neon excitation. Since high-velocity bombardment by both helium and neon ions provides excess energy, one could expect to see the same chemical shift in the second $K\beta$ satellite group in both helium and neon data in contrast with our observations. Furthermore, recoil and multiple L-shell ionization would probably cause significant alteration of the MO bonding structure compared to that calculated for ground-state atomic configurations. In conclusion, we do not have a tenable explanation of the large positive energy shifts observed for high-energy $K\beta$ satellites.

The decrease of the $K\beta$ energy shifts towards zero for the higher-energy satellites for both oxide and nitride excited by neon ions, as shown in Fig. 5, is another distinctive feature of the present work. ΔE_{SCF} calculations would predict a continued positive slope. It is presumed, however, that a highly ionized L shell and the resultant high charge (3, 4, or more electron units) suddenly created by ion impact can dominate the local electronic structure for both K and M orbitals. This would negate differences between the metal and compounds, causing the $K\beta$ shift to decrease. For the K x-ray energies to be affected by electron redistribution in response to the high-charge state, the outer-electron relaxation would have to occur in less than a K-hole lifetime of about 10^{-15} sec. The plasma frequency in Al metal is about 10^{-16} sec^{-1} and orbital times of outer electrons in oxygen are comparable, consistent with the interpretation given here. K-vacancy decay during outer-electron relaxation could lead to the peak broadening which is observed for the high-energy satellites.

Turning now to the oxide-nitride differences shown in Fig. 5, we note that the metal-nitride shift never becomes as large as the metal-oxide shift. This can be understood qualitatively from the smaller charge on an Al atom in AlN compared to $\mathrm{Al_2O_3}$. We note Domashevskaya and Ugai[24] have shown that, for electron excitation, the $K\beta$ parent-band peak in AlN is about 1 eV higher than in $\mathrm{Al_2O_3}$. Nefedow[25] found a smaller $K\alpha_{1,2}$ shift because Al in the nitride is less ionic than in the oxide. This smaller ionicity in AlN means that the effect of removing L-shell electrons on the $K\beta$ energy will be less in AlN than $\mathrm{Al_2O_3}$ as observed in the heavy-ion–produced $K\beta$ spectrum. Despite Al-ion recoil, the different chemical shifts for the oxide and nitride seem to imply that some effects of the ground-state electronic structure remain.

In summary, we have considered chemical shifts in Al K x-ray spectra associated with target atoms in their normal lattice sites as well as the probability and effects of Al recoil. Good agreement was obtained for the $K\alpha$ energy shifts in electron and light-ion excitation with ΔE_{SCF} calculations, where the compound formation in the oxide is simulated by removal of a single $3s$ electron. The same free-ion model, however, fails to predict the negative energy shift for the $K\beta$ parent line where solid-state effects shift the valence level in the oxide, but it does predict larger energy spacings between $K\beta$ satellites in the simulated oxide. Neon impact at 5 MeV is sufficient to produce a small Doppler broadening, but other effects resulting from recoil are the major contribution to the line broadening and appear responsible for reduced chemical shifts in the $K\alpha$ spectrum.

The $K\beta$ satellite energy shifts between oxide and metal are observed to change from negative to positive as the mass of the charged particle and the degree of L-shell ionization increase, but we are unable to arrive at a consistent rationalization of these $K\beta$ shifts. Further experimental work with other projectiles and different energies on more compounds appears desirable in order to obtain a better understanding of our limited observations. The present results also point to the need for an extended theoretical treatment incorporating both solid-state and multiple-ionization effects.

ACKNOWLEDGMENTS

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$6\,^3P_1$-$6\,^3P_0$ Excitation Transfer in Mercury, Induced in Collisions with N_2 Molecules[*]

J. Pitre,[†] K. Hammond, and L. Krause
Department of Physics, University of Windsor, Windsor, Ontario, Canada

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The cross section for the transition $6\,^3P_0 \rightarrow 6\,^3P_1$ in mercury, induced in collisions with N_2 molecules, has been determined by the method of delayed coincidences. The Hg $^3P_1$ state was excited by pulses of 2537-Å Hg resonance radiation and the decay of the long-lived 2537-Å afterglow was studied in relation to N_2 pressure. The resulting cross section $Q_{12}(^3P_0 \rightarrow {}^3P_1) = 4.18 \times 10^{-4}$ Å^2 was found to be in good agreement with the prediction of the principle of detailed balancing when compared with the cross section $Q_{21}(^3P_1 \rightarrow {}^3P_0)$. It was also found that, within the sensitivity of the method, collisions with N_2 molecules do not quench $^3P_1$ or $^3P_0$ Hg atoms to the ground state.

I. INTRODUCTION

The quenching of the $6\,^3P_1$ state of mercury by collisions with nitrogen and other molecules has been studied extensively, but it is only recently that agreement was reached between values of quenching cross sections obtained in different laboratories.[1,2] The available cross sections tend to encompass the total collisional deexcitation of the $6\,^3P_1$ state, which may proceed by way of two channels: transition to the metastable state ($^3P_1 \rightarrow {}^3P_0$) and to the ground state ($^3P_1 \rightarrow {}^1S_0$). Horiguchi and Tsuchiya[3] have recently reported separate cross sections for these two processes but the sum of the cross sections disagreed with the total values determined elsewhere,[1,2] in some cases by a factor higher than two. Samson[4] reported the only attempt to obtain the cross section for the process $^3P_0 \rightarrow {}^3P_1$ but his experimental results had to be subjected to large corrections for radiation trapping. A comprehensive investigation of the production of $^3P_0$ Hg atoms by collisions between the $^3P_1$ atoms and N_2 molecules, and the subsequent depopulation of the metastable state by collisions with N_2 molecules, ground-state Hg atoms and vessel walls, as well as by absorption of Hg radiation, was carried out by Bigeon,[5] who concluded upon the relative magnitudes of the various effects but obtained no corresponding cross sections.

In the present investigation, the $6\,^3P_0 \rightarrow 6\,^3P_1$ transition induced in collisions between $6\,^3P_0$ mercury atoms and N_2 molecules was studied by the method of delayed coincidences in the long-lived afterglow from an Hg-N_2 mixture irradiated with pulses of 2537-Å mercury resonance radiation. The method has the advantage that complications arising from pressure broadening and from absorption of other mercury radiation are effectively absent. With N_2 pressures appropriately chosen, the migration to the walls of the $^3P_0$ metastable atoms could also be impeded. Finally, the Hg vapor pressure employed (5×10^{-6} torr) was over 300 times lower than in previous experiments of other investigators and was confined to a region where the effects due to the imprisonment of mercury resonance radiation and to collisional deactivation of $^3P_0$ atoms by ground-state atoms were insignificant.

II. THEORETICAL

Figure 1 shows a scheme of the energy levels in mercury that are involved in the various processes of excitation and decay. The states $^1S_0$, $^3P_0$, and $^3P_1$ are denoted as levels 0, 1, and 2, respectively, and the transitions between them are indicated by arrows. Solid arrows correspond to collisional transitions and broken arrows to spontaneous radiative transitions. It is assumed that these are the only processes that cause the depopulation of any state. The transition rates are denoted by the symbols Γ, singly subscribed for radiative transitions and doubly for collisional transitions. The transition rates Γ_1 and Γ_2 are the reciprocal lifetimes of the appropriate states and, in the absence of radiation trapping, are constant, but the collisional transition rates de-