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Aluminum X-Ray Satellite Enhancement by Ion-Impact Excitation

A. R. Knudson, D. J. Nagel, P. G. Burkhalter, and K. L. Dunning
Naval Research Laboratory, Washington, D. C. 20390
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The impact of 5-MeV nitrogen ions on aluminum produces Al $K\alpha$ and $K\beta$ x-ray satellites not previously observed with other means of excitation. Comparison of measured and calculated x-ray energies shows that the satellites arise from Al ions with up to five L-shell vacancies.

X-ray lines produced by heavy-ion bombardment occur at higher energies than those generated by x-ray, electron, or proton excitation. Recently such shifts have been measured with semiconductor detectors[1-4] and Bragg spectrometers.[5,6] The observed increase in x-ray energy is ascribed to multiple ionization produced in the target atom by impact of heavy ions and the resulting increase in electron binding energies. In this Letter we report the measurement and interpretation of Al K x-ray satellites excited by nitrogen-ion impact. These satellites, some of them observed for the first time, dominate the normal $K\alpha_{1,2}$ and $K\beta_1$ radiation. This case of K-shell ionization in Al, a relatively light target atom, is readily understood in terms of additional L-shell vacancies produced by the nitrogen-ion impact.

An Al target 0.025 mm thick was bombarded at 45° incidence angle first with protons and then with singly ionized ^{14}N from the U. S. Naval Research Laboratory Van de Graaff operated at 5.0 MV. The resulting characteristic Al x rays were measured at 45° takeoff angle with a stepping Bragg spectrometer.[7] The collimator with blades 1.9 cm long and 0.125 mm apart, positioned between the target and spectrometer, and the pentaerythritol (PET) crystal ($2d$ spacing = 8.750 Å) set the resolution at about 3 eV in the region of Al $K\alpha_{1,2}$. The detector was a flow proportional counter with a 0.0042-mm Mylar window and a

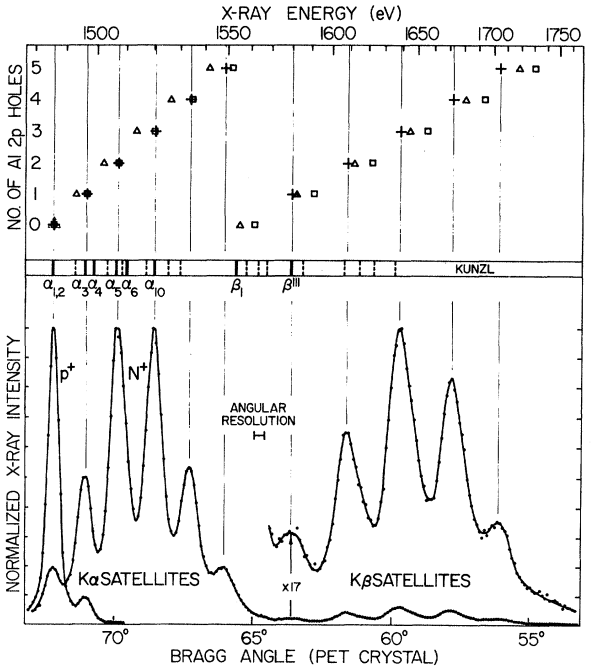

FIG. 1. Al $K\alpha$ x-ray spectra excited by impact of 5-MeV protons and nitrogen ions on Al metal. At the top, the measured peak energies (crosses) are compared with x-ray energies obtained from the Herman-Skillman program (squares) and the screening-constant program (triangles) of Veigele, Stevenson, and Henry, assuming $2p$ vacancies as well as the initial $1s$ vacancy. Energies of the $K\alpha_{1,2}$, $K\beta_1$ and satellite lines measured by Kunzl are indicated, with the stronger lines labeled and the weaker satellites shown by dashed lines.

Table I. Al K x-ray energies (eV) as measured and as calculated by the Herman-Skillman (HFS) program and the Veigele (SC) program.

Spectral Feature	Initial Hole Configuration	Measured	HFS Program	SC Program
$K\alpha_{1,2}$ line	(1s)	1486	1486	1486
$K\alpha$ satellites	$(1s)(2p)^1$	1496	1496	1493
	$(1s)(2p)^2$	1507	1507	1502
	$(1s)(2p)^3$	1521	1520	1514
	$(1s)(2p)^4$	1534	1535	1527
	$(1s)(2p)^5$	1548	1552	1542
$K\beta_1$ band	(1s)	-	1562	1555
$K\beta$ satellites	$(1s)(2p)^1$	1580	1591	1582
	$(1s)(2p)^2$	1609	1623	1612
	$(1s)(2p)^3$	1639	1657	1645
	$(1s)(2p)^4$	1672	1693	1680
	$(1s)(2p)^5$	1704	1732	1718

ton-excited spectrum (per unit beam current). gas mixture of 90% argon and 10% methane at 1 atm. Spectra were measured by step scanning over the desired angular region and accumulating counts for fixed values of integrated beam current at each spectrometer position. The spectrometer was controlled during runs by an SEL 840A computer which also processed the pulse-height distribution and printed the net intensity.

Figure 1 shows the Al K spectrum obtained with nitrogen-ion bombardment together with the spectrum resulting from proton excitation. The energy scale was calibrated by measuring the Al and Si $K\alpha_{1,2}$ line separation with proton excitation and using the x-ray–energy tables of Bearden.[8] Peak locations obtained by fitting asymmetric Gaussian curves to the data are given in Table I. Uncertainties in peak positions due to uncertainties in the results of the peak-fitting procedure and possible changes in the crystal lattice spacing with temperature are estimated to ±0.5 eV for the $K\alpha$ satellites and ±1.5 eV for the $K\beta$ satellites. The energies in Table I are in good agreement with results obtained in an earlier run using a crystal of ammonium dihydrogen phosphate ($2d = 10.642$ Å).-

The yield at the peak of the two most intense $K\alpha$ satellites was about 27 000 counts for 5 μC of $^{14}N^+$ ions. In the $K\beta$ part of the spectrum 20-μC runs were used. The measured net intensity at each spectrometer position was corrected for the detector efficiency (calculated window and gas absorption) which varied from 55% at 1486 eV (Al $K\alpha_{1,2}$) to 64% at 1704 eV, the position of the highest-energy satellite. The crystal diffraction efficiency may decrease with energy by about 20% over the range of Fig. 1, but available data[9] are too sparse now to warrant correction for this variation. No correction was made for self-absorption since the depth distribution of x-ray production is not known. Hence the spectra in Fig. 1 approximate the intensity escaping the target and not the intensity generated within the target.

The proton-excited spectrum consists of the normal $K\alpha_{1,2}$ peak and the $K\alpha_{3,4}$ satellite group. The $K\alpha_{5,6}$ group and other satellites have lower intensity and were not measured with proton excitation. However, the positions of the other Al satellites measured by Kunzl[10] using electron excitation and photographic recording are shown in Fig. 1.

With nitrogen-ion excitation the spectrum is radically different. A relatively weak line appears at the position of the normal $K\alpha_{1,2}$. The next two peaks line up with the $\alpha_{3,4}$ and $\alpha_{5,6}$ satellite groups. These two satellite groups have been ascribed to radiation from atoms which have, respectively, one and two initial L-shell vacancies in addition to the K-shell vacancy which is filled during x-ray emission.[11] This suggests that the

five peaks on the high-energy side of the $K\alpha_{1,2}$ line in the nitrogen-excited spectrum are $K\alpha$ satellite lines from atoms with one through five vacancies in the L shell.

In order to test this hypothesis, K x-ray energies were calculated for Al ions with zero through five L-shell vacancies by taking the difference in total electronic binding energy of the ion before and after the radiative transition. The required electron binding energies can be obtained from any of several programs. We used two: (1) the self-consistent Herman-Skillman,[12] Hartree-Fock-Slater (HFS) program and (2) the screening-constant (SC) program developed by Veigele, Stevenson, and Henry.[13] The total electronic binding energy was obtained by modifying the HFS program to calculate

$$E(\text{ion}) = \sum_i \epsilon_i + \tfrac{1}{2}\sum_i \langle i|-Z/r - V(r)|i\rangle,$$

$$\epsilon_i = \langle i|-\tfrac{1}{2}\nabla^2 + V(r)|i\rangle,$$

where i denotes the electrons present in the ion, Z is the atomic number, and $V(r)$ is the total self-consistent potential including exchange. The SC program calculates ionic energies by substitution of effective atomic numbers (calculated from screening constants) in the Dirac energy equation for each electron and then summing over electrons. The theoretical x-ray energies presented in Fig. 1 and Table I are absolute values free of any normalization.

In calculating the K-satellite x-ray energies, it was assumed that the L-shell vacancies were in the $2p$ level. Then the self-consistent HFS scheme gave results within 1 eV of experiment for all of the $K\alpha$ ($2p \rightarrow 1s$) lines except the last satellite which arises from atoms missing five L-shell electrons. HFS calculations for $2s$ vacancies, or combinations of $2s$ and $2p$ vacancies, did not give as good agreement with experiment. Holes in the $2s$ shell may be filled rapidly by Coster-Kronig transitions. McGuire's recent calculations of Coster-Kronig rates[14] can be used to show that, if $2s$ and $2p$ holes are created with equal probability, radiation from atoms with $2s$ vacancies would be less than 10% as intense as radiation from atoms with $2p$ holes. Hence, the SC program was run with the assumption of $2p$ vacancies, but it gave less satisfactory agreement with the $K\alpha$-satellite-peak energies as shown in Table I. However, in agreement with experiment and the HFS calculation, the SC program did indicate that the separation between satellite peaks increases with the number of L-shell holes.

Similar calculations were made for the $K\beta$ ($3p \rightarrow 1s$) band and its satellites. In this case, the SC method gave better agreement with the measured values than the HFS method. It is noted that calculations were made for free atoms while the data were obtained from a solid target. Taking the cohesive energy into account would lower the valence-electron levels and calculated x-ray energies by about 1 eV. Hence the discrepancy between theory and experiment for the $K\beta$ satellites is not due solely to solid-state effects.

For the $K\beta$ as well as for the $K\alpha$ satellites, both programs give separations between adjacent peaks close to those observed (about 12 eV for the $K\alpha$ satellites and 32 eV for the $K\beta$ satellites). Energy shifts calculated assuming a vacant M shell in a free Al ion were less than one half the observed shifts. Also, the M electrons are in the conduction band of the target and cannot be removed from one ion in the same manner as core electrons.

Kennard and Ramberg[11] state that removing both K-shell electrons would result in a shift of about 100 eV in the $K\alpha_{1,2}$ line of sodium. This suggested performing calculations assuming two $1s$ holes in addition to various numbers of $2p$ holes to see if the second grouping of satellites were indeed due to the ($3p \rightarrow 1s$) transition in singly K-ionized atoms rather than the ($2p \rightarrow 1s$) transition in doubly K-ionized atoms. The relative satellite spacing for two K-shell holes calculated with the HFS program was about 14 eV, considerably smaller than the observed peak separation of 32 eV in the second satellite group. It is also noted that the satellites in the second group have an average width of about 20 eV (full width at half-maximum) compared to a width of 8 eV in the first group and 4 eV for the proton-excited $K\alpha_{1,2}$ line. The higher-energy satellites include solid-state broadening and appear to have considerable multiplet splitting. The $K\alpha$ satellites are wider than the $K\alpha_{1,2}$ line as a result, in part, of their larger multiplet splitting.[11] $K\alpha_3$ and $K\alpha_4$ are part of the same multiplet, for instance, but are not resolved in the present experiment.

Less can be said about interpretation of the observed intensities than about their energies, but we can compare the intensities with proton and nitrogen excitation, the $K\beta/K\alpha$ ratios, and the relative peak intensities within the α and β groups. The integrated intensity of the entire nitrogen-excited spectrum is about one fifth that of the pro-

Dependence of the fluorescent yield on the degree of ionization would influence the relative intensities of spectra excited by heavy ions and point particles.[15]

Ordinarily, the $K\beta_1$ band is about 1% as intense as the $K\alpha_{1,2}$ line[16] since there is only one $3p$ electron compared to six $2p$ electrons and because of the smaller $(3p \rightarrow 1s)$ transition probability compared to $(2p \rightarrow 1s)$. With nitrogen-ion excitation, the integrated $K\beta$-satellite spectrum is about 7% as intense as the integrated $K\alpha$-satellite spectrum, even though the $K\beta$ satellites occur above the Al K absorption edge at 1560 eV and are hence reduced in intensity by self-absorption.

The relative intensities of satellites within the two groups together with a knowledge of the fluorescent yields for multiply ionized states would allow determination of the relative probability of producing the various initial, multiple vacancy configurations. Some of the time electron shake-off[17] will accompany the initial ionization mechanism, just as the L-shell vacancies leading to satellite emission with x-ray, electron, or proton excitation result from this process. The $K\beta$-satellite relative intensities differ from the relative intensities of the $K\alpha$ satellites by more than could be accounted for by variation in self-absorption.[18] Hence, the $K\beta/K\alpha$ intensity ratio is sensitive to the initial vacancy configuration, tending to increase with the degree of L-shell ionization.

A major point of the present work is to illustrate the advantage offered by heavy-ion excitation for the study of x-ray satellites. We agree with the interpretation[11] of the α_3-α_4, α_5-α_6, and α_{10} groups as being due to one, two, and three additional L-shell vacancies, respectively. Also, the β^{III} satellite has been shown to arise from the same initial configuration as the α_3-α_4 multiplet. The high intensity available with heavy-ion excitation allows investigation of satellites previously unmeasured or seen with only low intensity. Satellite emission from initial configurations missing four and five L-shell electrons are reported here for the first time. High-resolution measurements of the multiplet structure of Al K satellites are planned.

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