Dependence of the Ta K X-Ray Energy on the Mode of Excitation*

A. A. Hahn, K.-C. Wang, F. Boehm, H. E. Henrikson, and P. Vogel
California Institute of Technology, Pasadena, California 91125
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We have found that tantalum K x rays resulting from the K capture of ^{181}W to ^{181}Ta are lower in energy than the "normal" Ta K x rays produced by self-fluorescence in a tantalum source. The resulting shift, $E_{\text{W source}} - E_{\text{Ta source}} = -0.67(13)$, $-0.96(12)$, $-1.8(5)$ eV for the Ta $K\alpha_1$, $K\alpha_2$, and $K\beta_1$ lines, respectively. An interpretation in terms of a multiple-electron shake-off is presented.

The atomic K x rays represent an important and widely used energy-calibration standard as they are easily available and conveniently span the energy region up to 100 keV. With the use of crystal diffraction spectrometers, accuracies of a fraction of an electron volt are attainable. However at this level of precision one has to take into account the effects of the nuclear finite size and mass (isotope shifts) and of the chemical composition of the source (chemical shifts).[1,2] Furthermore, one should keep in mind that the K x-ray energy may depend on the method of excitation. We have investigated this problem for the two most commonly used x-ray excitations, fluorescence and electron capture. As a result of our studies, we find that the K x rays in Ta vary by as much as 1 eV.

The nuclear capture of a K-shell electron is known to represent a violent change in a previously stable electron cloud.[3] Several electrons may be shaken off, leaving the new atom in a statistically distributed ionization state at the time the K hole is refilled (emission of a K x ray). In the case of a heavy atom, weak hypersatellite lines with up to a 1-keV shift have been observed[4,5] as a consequence of the shake-off of the second K electron. Higher-level vacancies, while being more probable, give rise to smaller K x-ray shifts.

We have measured tantalum K x rays excited by two different processes. In the first case, the Ta x rays are produced by β^- electrons and low-energy γ rays emitted in the decay of ^{182}Ta to ^{182}W, exciting the tantalum atoms in the source by fluorescence. In the second case, the Ta x rays are produced in the electron capture of ^{181}W to ^{181}Ta.

The source material was 15 mg of natural Ta_2O_5 and 50 mg of WO_3 (7% ^{180}W). Both sources were uniformly spread over a 1-cm-diam circular area (Al_2O_3 powder was added to the former to facilitate an even distribution), and neutron-irradiated. The 2-m bend-crystal spectrometer system which is described in detail elsewhere[6] was used for this experiment. The two sources were mounted on a target wheel and could be turned alternately into position by a stepping motor. To eliminate drifts the sources were measured consecutively for each wavelength position of the spectrometer. Furthermore, each source was continuously rotated about its own axis to smooth out remaining azimuthal variations of the source distribution. To eliminate possible irregularities from source and crystal imperfection, data were taken in three independent setups, each of which required three to six weeks of time. The results are shown in Table I.

In setups No. 1 and No. 2, the source position

TABLE I. Observed energy shifts of the Ta K x rays from a ^{181}W source and a ^{182}Ta source. The quantities shown are $\Delta E = E_{\text{W source}} - E_{\text{Ta source}}$ and $\Delta\Gamma = \Gamma_{\text{W source}} - \Gamma_{\text{Ta source}}$ for a given tantalum x ray.

	Shift of centroid (eV)			Shift of width (eV)	
Setup No.	$\Delta E\ K\alpha_1$	$\Delta E K\alpha_2$	$\Delta E\ K\beta_1$	$\Delta\Gamma\ K\alpha_1$	$\Delta\Gamma\ K\alpha_2$
1	−0.67(13)	−0.99(15)	−1.5(1.1)	1.3(4)	0.7(3)
2	···	−1.19(29)	−1.9(6)		0.0(7)
3	···	−0.62(28)	···		0.7(7)
Mean	−0.67(13)	−0.96(12)	−1.8(5)	1.3(4)	0.6(3)

was varied (within the limitations of Bragg's law) so that different portions of the crystal were used. Irregularities of the source would be revealed by changes in the centroid shift. This was not observed, however. For setup No. 3, new Ta_2O_5 and WO_3 sources of slightly different thickness and distribution were prepared. We see that the results of runs 1, 2, and 3 are consistent. As an additional test we used two WO_3 sources as a null test. The result was a shift of 0.06(27) eV for the Ta $K\alpha_1$ line, consistent with zero.

Besides the shift of the K x-ray centroids we observed that the linewidth of the tungsten source is larger than that of the tantalum source. This is not unexpected since the shake-off process in the former is inherently statistical. However, no unfolding of the instrument linewidth was undertaken. The results are also shown in Table I.

The results may be semiquantitatively understood by using the following arguments. One expects that electron capture will cause more shake-off than fluorescence excitation. Hence the tantalum atoms from the tungsten electron-capture source will be more ionized. Intuitively one also expects that the ion with less electrons will have larger K x-ray energies, but our experimental result shows exactly the opposite. To explain this fact we have performed relativistic free-ion Hartree-Fock-Slater calculations[7] of the shifts of K x-ray energies. We expect that the electron configuration of the five-valent Ta (and six-valent W) is $Xe(4f)^{14}$. Therefore, we took this configuration as a basis. The calculated shift corresponding to the removal of one electron from each of the upper subshells is shown in Table II. We see that only the shake-off of $4f$ electrons corresponds in sign, magnitude, and ratios of the $K\beta_1/K\alpha_1$ shifts to our experimental results. Thus we conclude that the data are consistent with the shake-off of an average of 1.5 $4f$ electrons. Additional bound electrons are shaken-off with a considerably smaller probability.

Two comments are in order: The chemical composition of the targets is not the same; thus, chemical K x-ray shifts are in principle possible. However, our free-ion calculations (admittedly rather primitive for valence electrons) suggest that neither $6s$ nor $5d$ electrons can cause chemical shifts of the observed magnitude and of the observed pattern. The second comment concerns the time scale. The lifetime of the K hole is approximately 2×10^{-17} sec. A 40-eV electron (approximate $4f$ binding energy) can travel during that time a distance of ~ 1 Å. Thus, we conclude that the bound electrons have sufficient time to establish equilibrium; on the other hand, the time is too short for refilling of the outer vacancies from outside.

TABLE II. Calculated effect of the electron vacancies on the K x-ray energy. The change of the x-ray energy (in eV) caused by removal of one nl electron from the five-valent configuration $Xe(4f)^{14}$ is shown.

nl	$4f$	$5s$	$4d$	$4s$	$3d$
$K\alpha_1$	−0.43	0.78	0.04	4.55	1.37
$K\alpha_2$	−0.31	0.71	−0.09	4.09	0.55
$K\beta_1$	−1.63	1.40	3.27	8.25	32.19

Recently there has been a report[8] of a shift of the W $K\alpha_1$ x ray as produced by the β^- decay of ^{182}Ta. However, in this case the W $K\alpha_1$ x ray is primarily produced by electron conversion of the γ rays in $^{182}W^*$. Since the excited states of ^{182}W have nanosecond half-lives, all shake-off vacancies should have been long refilled before the $K\alpha_1$ emission. Bochert[9] has remeasured the W $K\alpha_1$ line from ^{182}Ta with a bent-crystal spectrometer in the Dumond geometry and has found no shift compared to the "normal" W $K\alpha_1$ x ray.

We have demonstrated that the energies of K x rays depend upon the mode of production. Therefore, in formulating new x-ray standards it is important to give due consideration to the production mechanism. It should also be noted that additional discrepancies in the energy standards now employed in x rays are present as has recently been pointed out in the literature.[10]

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Coherent On-Resonance Self-Focusing of Optical Pulses in Absorbers

H. M. Gibbs*
Bell Laboratories, Murray Hill, New Jersey 07974

and

B. Bölger
Philips Research Laboratory, Eindhoven, Netherlands

and

F. P. Mattar† and M. C. Newstein
Polytechnic Institute of New York, Farmingdale, New York 11735

and

G. Forster and P. E. Toschek
Institute of Applied Physics, University of Heidelberg, ‡ Heidelberg, West Germany
(Received 20 September 1976)

Self-focusing of spatially nonuniform coherent pulses has been seen in the center of Na and Ne transitions. Self-focusing and temporal reshaping were studied as a function of laser detuning in Na. The dependence of on-resonance self-focusing upon input pulse area was observed in Ne. Numerical solutions of the Maxwell-Bloch equations including transverse variations predict coherent self-focusing and yield a single parameter for estimating its importance for a given beam diameter and sample absorption.

Wright and co-workers[1] predict self-focusing (SF) that does not vanish on resonance and requires coherent propagation of spatially nonuniform pulses. Two experiments demonstrate this new effect with an increase of axial energy per unit area of 2 on resonance and 4.5 off. Self-induced transparency (SIT) outputs illustrate that resonance SF can dominate pulse reshaping in thick absorbers.

Coherent SF arises through the combined effects of diffraction and the nonlinear response of the medium. During the SIT reshaping regime little focusing occurs while each annular ring of the input Gaussian profile reshapes according to uniform-plane-wave SIT. Since the more intense inner rings propagate more rapidly, the tail of the pulse has more intensity in the outer rings. Diffraction into the forward central region (still in an amplifying condition) may result in an inward flow of energy.

The Maxwell-Bloch equations[2] whose numerical integration[1] revealed SF include radial variations and a time dependent phase:

$$E_+(z,\rho,t)=\xi(z,\rho,t)\,e^{i[\omega t-kz-\varphi(z,\rho,t)]};$$

$$\frac{\partial\xi}{\partial(\alpha z)}+\eta\frac{\partial\xi}{\partial(\alpha ct)}=-\left(\frac{2\pi\omega}{\alpha\eta c}\right)v-F\left[\xi\nabla_T{}^2\varphi+2\frac{\partial\varphi}{\partial\rho}\frac{\partial\xi}{\partial\rho}\right], \quad (1)$$

$$\xi\frac{\partial\varphi}{\partial(\alpha z)}+\eta\xi\frac{\partial\varphi}{\partial(\alpha ct)}=\left(\frac{2\pi\omega}{\alpha\eta c}\right)u+F\left[\nabla_T{}^2\xi-\xi\left(\frac{\partial\varphi}{\partial\rho}\right)^2\right], \quad (2)$$

$$\dot{u}=(\Delta\omega+\dot{\varphi})v-u/T_2', \quad (3)$$

$$\dot{v}=-\left(\frac{\kappa^2\xi}{\omega}\right)W-(\Delta\omega+\dot{\varphi})u-v/T_2', \quad (4)$$

$$\dot{W}=v\xi\omega-(W-W_0)/T_1, \quad (5)$$

where $\nabla_T{}^2=\partial^2/\partial\rho^2+1/\rho(\partial/\partial\rho)$, $\dot{u}=\partial u/\partial t$, $\rho=r/r_p$, r_p is the half-width at half-maximum (HWHM) radius of the laser beam, $\Delta\omega=\omega_{\text{atom}}-\omega_{\text{laser}}$, α