Anomalous Th M_3O_1 x-ray emission spectrum of ThO_2

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The Th M_3O_1 $(3p_{3/2}^{-1} \rightarrow 5s^{-1})$ x-ray emission spectrum of ThO_2 was measured with a high-resolution vacuum double-crystal spectrometer. The spectrum shows the first evidence of the splitting of a $5s$-hole level into two main structures which are due to a strong configuration interaction: $5s^{-1} \leftrightarrow 5p^{-1}5d^{-1}5(n,\epsilon)f$ super-Coster-Kronig process. The O_{1a} and O_{1b} hole energies of ThO_2 determined by the present measurements are, respectively, 293.9 and 276.2 eV. A large energy shift (order of ~ 15 eV) to lower binding energy from the theoretically predicted atomic energies is observed even when one takes into account the atom-oxide energy shift. The cause of the discrepancy is suggested to be due to a strong configuration interaction of the final $5p5d$ double hole: $5p^{-1}5d^{-1} \leftrightarrow 5d^{-3}5(n,\epsilon)f$.

I. INTRODUCTION

The dynamic correlation caused by the dipolar density fluctuation of a hole and the associated particle-hole excitation introduces a splitting and a large energy shift of a hole level. This results in a breakdown of the one-electron picture. This can occur when a single-hole level and two-hole–one-particle level are degenerate (or nearly degenerate) and strongly coupled to each other.[1,2] Such many-electron effects were observed in the $5p$ x-ray photoelectron spectroscopy (XPS) spectra of the actinide metals and compounds,[3-5] namely, splittings in the $5p_{3/2}$-hole level and a large energy shift of the $5p$-hole levels from the relativistic Hartree-Fock (HF) change in self-consistent field (ΔSCF) hole energies. Sham and Wendin[5] gave a qualitative explanation of these anomalies in terms of configuration interaction (CI) between the $5p$ hole and the $5d^{-2}5f$ excitation or in terms of dynamic correlation between dipolar density fluctuation of a $5p$ hole $(5p^{-1} \leftrightarrow 5d^{-1})$ and $5d$ electrons $[5d^{-1} \leftrightarrow 5(n,\epsilon)f]$. They proposed shake-up to low-lying $5f$ levels and super-Coster-Kronig fluctuations of the core hole for the satellite features of the spectrum. Boring, Cowan, and Martin[6] performed the relativistic HFCI calculations for the $5s$-$5p$ XPS spectra of metallic elements Ra($Z = 88$), Th($Z = 90$), and U($Z = 92$), obtaining excellent agreement with the experiment. They showed that the major satellite features in the $5p$ spectrum of metallic Th can be accounted for by an atomic model[6] because of the localization of the many-body processes on the same atomic site. Recently, the one-particle Green's-function calculation was performed by one of the present authors for the $5s$-$5p$ XPS spectra of metallic elements Ra and Th.[7] This calculation, which also is in good agreement with experiment, includes explicitly the continuum interaction that was neglected in the CI calculations. However, it was shown that the effects of the interaction with the continuum were small in most of the cases considered.

The theoretical studies[6,7] also show that the $5s$-hole level also should be strongly influenced by the $5s^{-1} \leftrightarrow 5p^{-1}5d^{-1}5(n,\epsilon)f$ super-Coster-Kronig (SCK) fluctuation or configuration interaction. The CI calculation by Boring et al.[6] predicts that the $5s$-hole level should be split into three structures: namely, two levels below threshold and one level above threshold, the latter of which takes nearly half of the original strength. The one-particle Green's-function calculation[7] predicts that the $5s$-hole level will be split into two structures: one prominent peak below threshold and the broad nonresonant [≈ 14 eV full width at half maximum (FWHM)] structure above threshold. The XPS data for the $5s$ level are not available to date. However, some preliminary measurements[8,9] show three overlapping peaks extending over about 20 eV (Ref. 8), and a weak feature appearing at around 290 eV at very low resolution for ThO_2.[9]

When the experimental XPS spectrum for a certain core level is not available or is distorted because of a large background, the x-ray emission spectroscopy (XES) spectrum involving the core-hole level of interest is a useful and promising alternative for the study of the dynamics of the core hole. In particular, when the initial core hole is well defined, the XES spectrum often reflects essentially the shape of the spectra function of the final-state hole.[10] Because of its relatively featureless background the XES spectrum which involves the core-hole level of interest as the final-state hole, is very useful in the study of many-electron effects.[11] In order to study the many-electron effects of $5s$ core-hole level of Th, we measured the M x-ray emission spectrum of ThO_2 in the present work.

II. EXPERIMENT

The Th x-ray emission spectrum was produced by direct electron excitation in a demountable x-ray tube.[12] The bombarding electrons are incident normal to the anode and the observed photons are those that emerge along the same normal. The anode target was prepared by rubbing
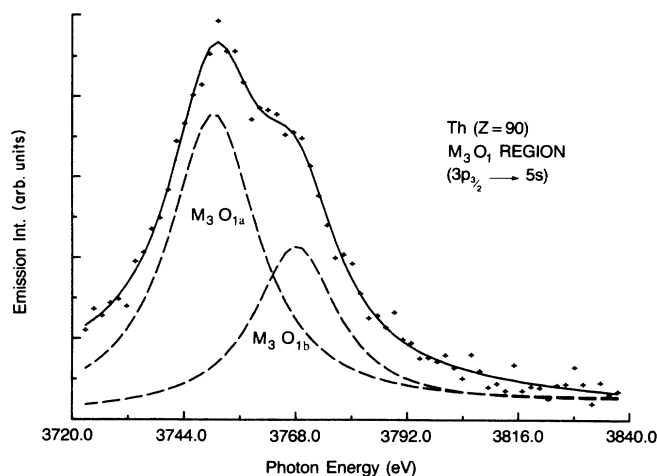
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FIG. 1. The (+) points are the experimental spectrum of Th[(ThO)$_2$] in the M_3O_1 region. The solid line is the least-square-fitted profile using a model of two Lorentzian components. The dashed lines are the individual components designated M_3O_{1a} and M_3O_{1b}.

finely ground reagent grade ThO$_2$ on a copper anode that had previously been roughened with a coarse abrasive. The emission spectrum was obtained with a vacuum double-crystal spectrometer[13] equipped with high-quality germanium (111) crystals ($2d_\infty$ =6.53308 Å at 22.5°).[14] The radiation was detected by a flowing gas proportional counter using P10 gas (90% argon + 10% CH4) at a pressure of 0.53 kPa (400 Torr). The x-ray tube operated at 12 kV and 110 mA during the measurements.

The x-ray spectra being reported are the Th $M\gamma(M_3N_5)$ and M_3O_1 from ThO$_2$. We also measured Ca $K\alpha_{1,2}$, an impurity in the sample, to set the energy scale in the M_3O_1 region. Corrections[14] for crystal temperature, vertical divergence, and index of refraction were applied to determine the Bragg angle. The uncertainty of the experimental energy scale (±0.06 eV) is primarily due to counting statistics and modeling of the spectral lines. The diffraction profile in the parallel (1,−1) position has a FWHM of 0.70±0.03 eV which is taken as the instrumental line broadening. The Th M_3N_5 peak position is 3367.9±0.2 eV with a FWHM of 13.9±0.5 eV. The accepted value[15] of the M_3N_5 line is 3669±2 eV. The Ca $K\alpha_1$ peak position is 3691.35±0.05 eV which is about 0.5 eV less than the accepted value[15] of 3691.81±0.05 eV. The energy scale in Fig. 1 was set relative to the present Ca $K\alpha_1$ measurement.

III. RESULTS AND DISCUSSION

The XES in the M_3O_1 region was fit via a nonlinear least-squares routine[16] modeling the spectrum with two Lorentzian profiles and a background. In Fig. 1, we present the measured spectrum, overall fit, and resolved components designated M_3O_{1a} and M_3O_{1b}. The M_3 hole energy of ThO$_2$ (4044.1 ± 0.2 eV) is determined by using the measured M_3N_5 XES emission energy (3367.9 ± 0.2 eV) and the N_5 XPS hole energy of ThO$_2$ (676.2 eV)

measured by Fuggle et al.[8] The O_1 energies of ThO$_2$, determined by the present measured $M_3O_{1a,b}$ XES emission energy (3750.2, 3767.9±0.5 eV), are 293.9 and 276.2 eV, respectively. The widths (FWHM) of the $M_3O_{1a,b}$ components are 23.1±1.5 and 21.7±2.0 eV, respectively, with an intensity ratio of b/a =0.55.

The XPS energy shift between ThO$_2$ and metallic Th observed for the N, O, and P core-hole levels range from 0.7 to 2.1 eV.[8] We assume that the metal-oxide energy shift is about 1.5 eV (to within an accuracy of about 1.0 eV). Taking the atom-metal energy shift at 9.5 eV as calculated by Johansson and Mårtensson,[17] we obtain the atom-oxide energy shift of +8.0 eV. Thus, the estimated atomic $O_{1a,b}$ hole energies are 301.9 and 284.2 eV. The estimated widths of the two structures are ≈14.5 and 13.1 eV, respectively, assuming the M_3 width to be the same as for metallic uranium (8.6 eV).[18]

The HFCI calculation by Boring et al.[6] predicts one level at 317 eV (0.48 of the original unit strength), a second at 298 eV (0.21), and a third at 293 eV (0.23). The Green's-function calculation by one of the present authors[7] predicts one nonresonant broad spectrum (14 eV FWHM) centered at 314 eV (0.65) and a second prominent peak at 267 eV (0.35).[19] The intensity ratio of the two structures by the HFCI calculations is 0.9, and by the Green's-function method it is 0.54. Although there is a large energy shift between the present measured energies and theoretical energies, the above-mentioned results imply that the broad peak at 293.9 eV (M_3O_{1a}) corresponds to the broad nonresonant structure with mainly 5s-hole character above the $5p_{3/2}^{-1}5d^{-1}$ threshold 307.7.[6] The physical threshold of $5p_{3/2}^{-1}5d^{-1}$ would be shifted to lower than the calculated value because of further many-electron effects in the double-hole state, as discussed later. The structure peaked at 276.2 eV (M_3O_{1b}) consists of many multiplet levels split off from the main line due to strong configuration interaction $5s^{-1} \leftrightarrow 5p^{-1}5d^{-1}$ (super-Coster-Kronig process) with mainly $5p^{-1}5d^{-1}5f$ character. These split levels are not experimentally discerned because they are broadened by the lifetime of the initial M_3 hole, estimated to be about 9.0 eV and overlap each other. The peak above the threshold has mainly the character of the 5s-hole level with about 65% of the original strength, and the peak below the threshold with $5p^{-1}5d^{-1}5f$ character has about 35% of the original strength of the 5s-hole level. There are large energy shifts between the present measured O_1 hole energies and the theoretical predictions. This implies that some important aspects have been neglected in the theoretical formulation.[6,7]

(A) The atom-oxide energy shifts: The effect of the dipolar density fluctuation of a 5s hole is to introduce a nonspherical (hole-hopping) correlation between dipolar distortions of the charge densities of the 5s hole and the 5d shell. The screening (relaxation) time of this hole-hopping correlation is given by the dipole relaxation energy shift (approximately equal to a difference between the HFΔSCF and experimental ionization energy). In order for the screened state to be meaningful, the decay time must be relatively long in comparison to the screening time, i.e., the line shift must be considerably larger than

the linewidth. Otherwise, the screening is incomplete. From this viewpoint, a number of quasidiscrete levels below threshold can be considered to form a screened state. However, in the nonresonant state above threshold there will be a competition between the decay of a 5s hole and screening. In other words, when the 5s-hole level is split into a number of quasidiscrete levels and a continuum, due to dissipation during the screening process, only the screened state of a 5s-hole level will remain in these quasidiscrete levels. Thus, we may expect different atom-solid energy shifts for these two main structures, since the atom-solid energy shift was calculated by using the complete screening model and $Z+1$ approximation which makes it possible to introduce a Born-Haber cycle to connect the initial state with the final state of the core ionization process.[17] However, in the case of 5p XPS spectrum of Th, the atom-solid energy shifts of 9.5 eV (Ref. 7) and 11.0 eV (Ref. 6) are introduced to compare atomic data with the metallic data. There was no large discrepancy between theory and experiment. The previous studies of 4p XPS spectra of the elements Pd to Xe (Refs. 1 and 2) show that the decay of a 4p hole is actually so rapid that the screening process becomes incomplete. However, the good agreement between theory and experiment is obtained by using atom-solid energy shift calculated in the same way. Then one may conclude that the deviation due to the atom-solid energy shift is much smaller than the deviation observed in the present work.

(B) In the theoretical treatments considered so far,[6,7] many-electron effects of the final double-hole state were neglected. As in the case of a single 5p-hole excitation, one can expect a very strong configuration interaction between the $5p^{-1}5d^{-1}$ double-hole level and $5d^{-3}5(n,\epsilon)f$ triple-hole–one-particle level. One may expect splittings and large energy shifts of the multiplet levels. Such anomalous effects were already observed experimentally and studied theoretically in the case of $M_{4,5}$-$N_{2,3}N_{4,5}$ Auger transitions of the elements Pd to Xe.[20-22] It was shown that in the elements around Sn($Z=50$) the quasiparticle picture of double 4p4d hole breaks down completely due to the $4p^{-1}4d^{-1}\leftrightarrow4d^{-3}4(n,\epsilon)f$ process.[20] Even in the case of Xe where there is a discrete structure,[21] the Auger energies are shifted as much as ≈17 eV from the relativistic Hartree-Fock ΔSCF energies and the energy shift differs for different multiplet levels.[22] This energy shift is interpreted as due to the $4p^{-1}4d^{-1} \leftrightarrow4d^{-3}4(n,\epsilon)f$ process. The recent Green's-function calculation[22] gives an excellent agreement with experiment. From the Green's-function method, the self-energy of the initial hole can be modified appreciably by many-electron effects of the final double-hole state.[23] The self-energy will be modified by the spectral function of the final double-hole state. The behavior of the self-energy in the energy region of interest may change drastically when the many-electron effects of the final double-hole state are strong, leading to a large change in the spectral function

of the initial hole. In the present case, because of anomalous splitting of a 5p-hole level (in the case of the single-hole excitation), it is extremely difficult to make a qualitative analysis of the many-electron effects on the 5s-hole level. One should note that interpretation of the 5s-hole level spectrum may depend critically on many-electron effects of the final 5p5d double hole. For the 4s XPS spectrum of Xe, one can expect a similar many-electron effect because of the final 4p4d double-hole state which involves a 4p hole. However, for the 4s hole, the 4s ΔSCF-hole level energy lies far enough from the $4p^{-1}4d^{-1}$ threshold that many-electron effects will not influence the spectrum.[1,2] This is in contrast with the 5s-hole level, where the 5s ΔSCF-hole energy of 308.6 eV (Ref. 6) and the $5p_{3/2}^{-1}5d^{-1}$ threshold energy of 307.7 eV (Ref. 6) suggests that the self-energy around the $5p^{-1}5d^{-1}$ threshold will be modified appreciably.

(C) As in the case of Ba,[24,25] the $5p^{-1}5d^{-1}5f$ configuration has to be calculated within the ΔSCF scheme so the $5d^{-1}5f$ and $5p^{-1}5f$ Coulomb interaction can be screened, and relaxation in the presence of 5f electron can be included. Furthermore, the multiplet structure of the $5p^{-1}5d^{-1}5f$ configuration has to be taken into account completely. These aspects were neglected in the Green's-function calculation.[7] Inclusion of screening of the $5d^{-1}-5f$, $5p^{-1}-5f$ Coulomb interaction would increase the energies of the two splitting to higher binding energies. Preliminary results show that one can obtain approximately the lower binding energy level, but at the same time one obtains a higher binding-energy level for the structure above threshold.

IV. SUMMARY

The Th M_3O_1 XES spectrum was measured and found to consist of two components, M_3O_{1a} and M_3O_{1b}, and the two 5s-hole level energies were extracted from the experimental data. The two main structures of a 5s-hole level observed are shifted from theoretically predicted positions. This difference is suggested to be due to strong many-electron effects of the final 5p5d double-hole state. We leave to the future the Green's-function calculation which would include the many-electron effects of the final 5p5d double-hole state; i.e., the strong configuration interaction between 5p5d double hole and $5d^{-3}5(n,\epsilon)f$ triple-hole–one-particle state.

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