Determination of the lifetime width of the argon L_1-hole state

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The width of the argon 2*s* level was experimentally obtained from x-ray emission-spectroscopy (2.25±0.15 eV) and x-ray photoelectron-spectroscopy (XPS) (2.25±0.05 eV) measurements. A theoretical value of 1.85 eV was obtained by a Green's-function calculation. A high-energy satellite located 2.7±0.2 eV above the L_1-$M_{2,3}$ x-ray emission transition was confirmed and identified as the $2s^{-1}3p^{-1}\rightarrow 3p^{-2}$ double-hole transition. The XPS measurement of the argon 2*s* ionization energy gave a value of 326.25(5) eV.

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I. INTRODUCTION

Lifetime broadening of spectral lines and observation of satellite structures in core-level spectroscopies are directly observable manifestations of the relaxation of core hole states. In the case of x-ray photoelectron spectroscopy (XPS), when all satellite lines associated with a particular hole excitation are known (which is usually not the case), the relaxation shift can be determined from experimental data. Otherwise, the shift has to be determined with the help of theoretical calculations. Many efforts have been made to determine ionization energies experimentally and to calculate them accurately. However, to date not much attention has been paid to the problems of lifetime broadening. A decade ago, Fuggle and Alvarado [1] showed that, for a large number of elements, there are large discrepancies (by as much as a factor of 2 to 3) between experimental and theoretical hole-state widths calculated by McGuire [2] and Chen, Crasemann, and Mark [3]. One of the hole states that showed such large discrepancies is the L_1 state of the elements from Ar ($Z=18$) to Kr ($Z=36$). Since then, Ohno has calculated the L_1 XPS spectra from first principles using the Green's-function method [4]. As in other applications of this method to the hole states of elements over an extended range of the periodic table, there is an improvement in agreement between experiment and theory [5]. The main decay channels for the L_1 hole state are the L_1-LM Coster-Kronig (CK) processes. For the 3*d* transition elements up to Co ($Z=27$), better agreement with experiment was found by calculating the linewidth using a less attractive potential. This implies that solid-state effects like the delocalization and dynamical screening of two-hole final states become significantly important. It was suggested that the decrease of the L_1 widths at Ni ($Z=28$) is probably due to the transition of CK processes from the delocalized solid-state behavior to the localized atomiclike behavior for the elements $Z\geq 28$. The ideal systems for a comparison between atomic lifetime calculations and experiment are the monatomic rare-gas elements. The experimental L_1 level width of Kr with a binding energy of 1923.7 eV [6] is not at hand to compare with theory, but the more accessible argon ($Z=18$) L_1 level width is available. The reported experimental argon L_1 lifetime widths differ by 50% [7]. An improvement of the accuracy of the experimental L_1 width of argon can serve to test the atomic calculation of the L_1 width.

In the present work, we report two separate experimental measurements of the argon L_1 level width. We determined the L_1 width from a remeasurement of the L_1-$M_{2,3}$ x-ray emission-spectroscopy (XES) spectrum with improved instrumentation, as well as from the remeasurement of the XPS spectrum of the argon L_1 with improved statistics from the earlier measurements [6]. We also present the theoretical width using a more accurate Green's-function calculation than in the previous estimate [4].

II. EXPERIMENT

A. XES

The soft-x-ray emission spectrum of argon in the L_1-$M_{2,3}$ region was obtained with a grazing-incidence spectrometer that has been described in [8]. A continuous flow of argon gas kept the pressure at 2 Torr in a gas cell, mounted in a differentially pumped collision chamber. The sample gas was excited by electron impact of 5-keV electrons, from a two-stage electron gun with a tungsten filament and a LaB_6 cathode.

The grazing-incidence spectrometer provides a choice of three different fixed gratings and a moveable two-dimensional MCP (multichannel-plate) detector whose efficiency is enhanced by a CsI coating and an applied capturing electrode. The spectrometer was separated from the source by a self-supporting silver foil 1200 Å thick. The foil separated two individually pumped vacuum chambers. Another important function of the foil was to reduce the background level by filtering the uv radiation from the source. The spectrum was obtained with a 400-lines/mm grating and a 10-μm slit. The instrumental configuration of the spectrometer did not have as high resolution as the previous measurement by Nordgren *et al.* [7], who recorded the spectrum photographically, but the improved instrumentation permitted a more reliable determination of the line profile and

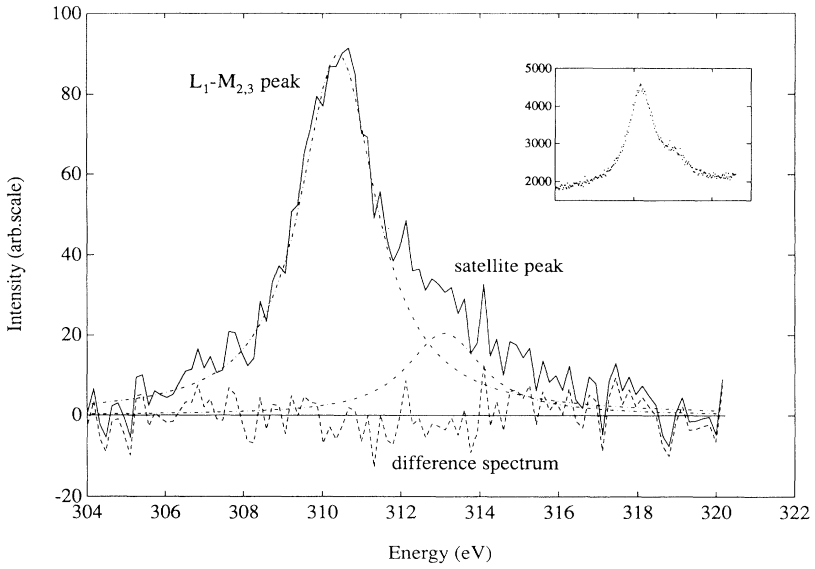

FIG. 1. Inset shows the x-ray emission spectrum of argon in the L_1-$M_{2,3}$ energy region. Since the energy scale was not sufficiently calibrated in that spectrum, another spectrum (solid curve in the large figure), with poorer statistics, was used to extract the inherent linewidth. A linear background has been subtracted from the solid-curve spectrum. The dash-dotted curves show the Voigt profiles with Lorentzian widths of 2.25 eV and Gaussian widths of 0.4 eV (the same width for both peaks was assumed). The dashed curve gives the difference between the experimental curve and the Voigt profiles.

therefore a more reliable estimate of the inherent lifetime width. The energy scale was calibrated using the $L_{2,3}$ XES spectrum of copper recorded in third order.

Figure 1 displays the L_1-$M_{2,3}$ spectral region consisting of the main diagram line and a weaker high-energy satellite on a high background. Since the Coster-Kronig decay channel totally dominates for the 2s hole decay, the radiative emission signal is weak, giving a low signal-to-noise ratio. The two features were modeled with two Voigt profiles on a linear background. Equal width for both peaks was assumed. The Gaussian portion, representing the experimental window function, was constrained to a FWHM (full width at half maximum) of 0.4 eV. For the Lorentzian part, corresponding to the natural lifetime width, a FWHM of 2.25 eV was obtained. We estimate the probable maximum error for the Lorentzian part to be ± 0.15 eV. The uncertainty in the Gaussian width can be neglected in the determination of the Lorentzian width, since the experimental window function is much narrower than the inherent linewidth. The primary factors contributing to the uncertainties are the limited statistics and the difficulty of correcting for the background. Other factors that can affect the results are satellite lines in the near vicinity of the main line and Lorentzian-like contributions to the experimental window function. In conclusion, we obtain from the XES a lifetime width of 2.25 ± 0.15 eV. The position of the satellite peak is 2.7 ± 0.2 eV above the main peak (L_1-$M_{2,3}$). The corresponding separation in [7] is 2.9 eV, which is in good agreement with the present experiment. Evidence of the final-state doublet $3p_{1/2,3/2}$ with a spin-orbit split of 0.18 eV [9] is not apparent from the symmetric profile of the L_1-$M_{2,3}$ spectral line. This is reasonable since the spin-orbit splitting is an order of magnitude less than the corrected linewidth. No further correction for final-state breadth was applied.

B. XPS

The XPS spectra were obtained with a photoelectron spectrometer that utilizes monochromatized Al $K\alpha$ (1486.7-eV) x-rays for excitation. Scans were made of the Ar 2s and Ar 3s line regions in this experiment. The FWHM of the Ar 3s line was 0.37 eV, which is taken as the FWHM of the spectrometer function. The total width of the spectrometer function is small compared to the total FWHM of the Ar 2s electron line. Curve fitting of the 2s line with a Voigt profile constrained for the 0.37-eV Gaussian spectrometer contribution gives a negligible decrease of 0.04 eV to the experimental width. Figure 2 shows a fit of a Lorentzian and a straight-line background function to the spectrum. The background in the spectrum is due to a dark current in the detector and an underlying continuum associated with argon 2p ionization. In comparison, the dark current is negligible and therefore the background is essentially originating from the 2p shakeoff, and, as expected, the shakeoff level is higher on the low-energy side of the line. Several mod-

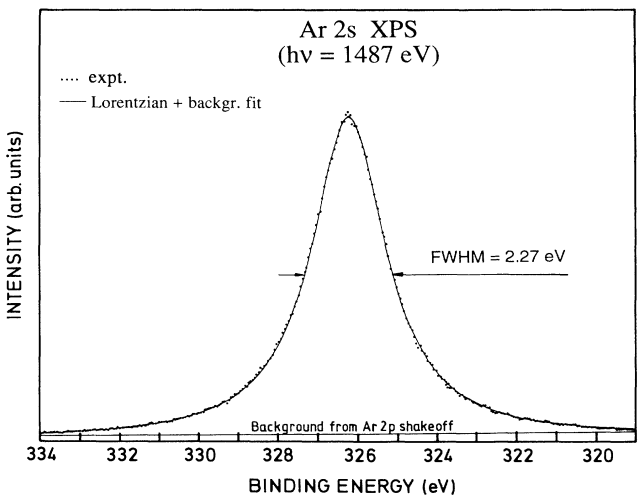

FIG. 2. Ar 2s x-ray photoelectron spectrum. A monochromatized Al $K\alpha$ source was used for excitation. Note that the background level is higher at the low-binding-energy side of the 2s line. This is due to the sloping Ar 2p shakeoff intensity.

el fits were made using various assumptions for the background. However, all attempts gave linewidths within 0.02 eV. The FWHM of the Lorentzian function fitted to the Ar 2s line is 2.27±0.02 eV. This value determines an upper limit for the natural linewidth. In order to obtain the lower limit, several assumptions have to be made. If the spectrometer function can be regarded as a Gaussian function, our results indicate an inherent linewidth that is a few hundredths of an eV smaller than 2.27 eV. The accuracy of the determined value is, to a large extent, dependent on the fitted background, and therefore the error limits are larger than ±0.02 eV. When considering all different trials, using different assumptions for the background, we conclude an XPS value for the inherent linewidth of 2.25±0.05 eV for the argon 2s line.

III. RESULTS AND DISCUSSION

The energy scale of the L_1-$M_{2,3}$ XES in Fig. 1 is relative to a copper $L_{2,3}$ spectrum recorded in third order. The absolute energy scale may possibly have some uncertainty. Therefore, XES is not used to derive the binding energy of the argon L_1 (2s). However, the relative scale in the XES spectrum should be fairly good since the spin-orbit splitting between L_2 and L_3 is known quite accurately for copper. The experimental ionization energy of the 2s level of 326.25±0.05 eV in Table I is from the XPS measurement.

In Table I, theoretical ionization energies calculated by different approaches are listed. A more complete summary of theoretical ionization energies are given in [10]. As discussed before [4], for free atomic argon, the dipole (hole-hopping) relaxation shift is negligible because of the absence of the L_1-$L_{2,3}M_{4,5}$ CK processes. The ground-state correlation shift is also expected to be negligible. This explains the good agreement between experiment and Dirac-Hartree-Fock (DHF) Δ SCF results. When the dipole (hole-hopping) relaxation shift is not negligible, the DHFΔSCF method does not accurately predict the ionization energies.

In Table II, the previously reported experimental and theoretical 2s level width of argon and the values of this report are listed. The experimental width of 2.6 eV is from an early XPS measurement uncorrected for instrumental broadening. Mehlhorn [11] extracted a width of 1.84±0.2 eV from AES (Auger electron spectrum) of the L_1-$L_{2,3}M_{2,3}$ Coster-Kronig peak. From a high-resolution XES study of gaseous argon, using photographic detection, Nordgren *et al.* [7] obtained an estimate of the 2s width of 1.3 eV. The present 2s level width of 2.25±0.15 eV from XES and 2.25±0.05 eV from XPS are in good agreement, eliminating the discrepancy between the measurement of the 2s level width from the XES and XPS experimental techniques. Comparison with the AES estimate of 1.84±0.2 eV is not within the uncertainties. The discrepancy could be due to difficulties in extracting the inherent linewidth from the AES spectrum, since the *LLM* Coster-Kronig peak consists of several transitions overlapping to give a broad structure.

TABLE I. Ionization energy of the 2s level of argon (in eV).

Experiment	Theory
326.3(37)[a]	326.8[c]
326.25(5)[b]	326.9[d]
	326.6[e]

[a]The XPS value is taken from [14].
[b]This is the XPS value obtained in the present work.
[c]This is the DHFΔSCF value from [15].
[d]This is the g-Hartree value from [16].
[e]This is the value obtained using the Green's-function method taken from [4].

TABLE II. Widths of argon 2s level in (eV).

Experiment		Theory	
Present work	Others	Present work	Others
XES 2.25(15)	1.3[a]	1.85	1.3[d]
XPS 2.25(5)	1.84(20)[b]		1.63[e]
	2.6[c]		2.6[f]
			2.7[g]

[a]XES value from Ref. [7].
[b]AES value, Ref. [11].
[c]XPS value, Ref. [6].
[d]Reference [4].
[e]Reference [13].
[f]Reference [2].
[g]Reference [3].

The previously reported theoretical widths were obtained using different approximations for the potential and wave function. These early estimates differ from experiment by about 40%. A discussion of the different theoretical approaches has been given earlier [4]. Ohno obtained a 2s level width of 1.3-eV width using the extended RPAE (random-phase approximation with exchange) Green's-function method [4]. An improvement in the accuracy of the Green's-function calculation for Ar was made by taking into account some decay channels that were underestimated previously. The resulting width of 1.85 eV corresponds better to the present experimental width.

The satellite on the high-energy side of the L_1-$M_{2,3}$ diagram line in Fig. 1 is designated as the double-vacancy transition $2s^{-1}3p^{-1}\rightarrow 3p^{-2}$. We calculated the average initial- and final-state energies by the DHFΔSCF method using the computer code by Grant *et al.* [12]. Since the ground-state correlation and certain other kinds of relaxation are totally neglected by the DHFΔSCF method, we estimate these contributions for double holes by simply taking a linear sum of the discrepancy between experimental and DHFΔSCF results for the single-hole ionization energy. The calculated $2s^{-1}3p^{-1}\rightarrow 3p^{-2}$ average satellite energy is 2.5 eV above the main line and is in good agreement with the experimental position of 2.7±0.2 eV above the main line.

IV. CONCLUSION

The argon 2s level width has been obtained by two separate experiments, XES and XPS, with improved in-

strumentations. An experimental $2s$ level width of 2.25 eV was obtained. A calculation from first principles using the Green's-function method gave a $2s$ level width of 1.85 eV, which is in reasonable agreement with the present experimental values. A high-energy satellite to the L_1-$M_{2,3}$ diagram line is identified as a double-vacancy transition $2s^{-1}3p^{-1} \rightarrow 3p^{-2}$. This identification is supported by a calculation of the transition energy that positions the transition 2.5 eV above L_1-$M_{2,3}$ compared with the experimental value of 2.7 ± 0.2 eV. From XPS, an ionization energy for the $2s$ level of 226.25 ± 0.05 eV was obtained.

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