Resonance absorption at the L edges of tantalum: The white line

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The x-ray absorption spectrum at the L edges of tantalum has been measured on two spectrometers that are equipped with: (i) a conventional bremsstrahlung source and a LiF(200) crystal, and (ii) a synchrotron source and a channel-cut Si(220) crystal. Our results are similar to those reported by earlier workers except that the apparatus (ii) yields a Ta L spectrum of the highest resolution reported thus far. Of particular interest is the sharp spike (white line) occurring at the L_{III} and L_{II} but not at the L_I edge. We associated the white line with an atomiclike allowed transition from the $2p_{3/2}$ or $2p_{1/2}$ state to the vacant $5d$ states of a high density. However, a quantitative comparison with the calculated band structure can not be made because none of the existing calculations has included the effect of a core hole. In an attempt to understand the white lines, we present two least-squares analyses of the Ta L_{III} edge in terms of (a) a Lorentzian profile and (b) a Breit-Wigner-Fano-type formula. The latter, which was first suggested by Cauchois and Mott, appeared to provide a better fit to the asymmetric line shape.

I. INTRODUCTION

The general status of our knowledge on x-ray absorption spectra has recently been reviewed by several authors.[1-4] Historically[1], the absorption feature occurring just above the edge on the high-energy side was referred to as the Kossel structure, while that occurring at ~50 eV and above the edge was called the Kronig structure. The theory and experiments on the Kronig structure, also known as the extended x-ray absorption fine structure (EXAFS), have been well studied by a number of workers.[5-11] For a given absorbing atom, the EXAFS was attributed to an interference effect of the emerging photoelectron backscattered from the surrounding atoms. Near the edge, the Kossel structure was expected to reflect the distribution of unoccupied quantum states for the absorbing atom. However, due to the presence of a very-short-lived core hole, the final-state wave function could not be easily defined. In view of this difficulty, most of the interpretations of the near-edge structure have been speculative in nature.[1]

The appearance of a strong peak just above the x-ray absorption edge for some elements and compounds has been an interesting subject in x-ray spectroscopy for many years.[12-28] The strong peak is referred to as a "white line" (or "raie blanche" in French), because such a little amount of radiation at certain wavelengths would penetrate the absorber relative even to the radiation transmitted above the edge, giving a white line on the photographic film used in the early experiments. For example, white lines have been observed at the K edges of elemental Ga and As, Ni in Ni_2O_3, Cu in CuO, and Zn in ZnO,[17] but not in the $3d$ transition elements.[29] White lines have also been observed at the L_{II} and L_{III} edges (but not at the L_I edge) of Fe, Co, Ni,[18,24] Cu in CuO,[19] Ru, Rh, Pd,[20,21] Sm,[26] Gd through Lu,[25] Ta, W, Re,[12-16,23] compounds of Hg and Tl,[22] and U.[13] The list is by no means complete; in fact, with the enhanced intensity and improved resolution from synchrotron radiation sources,[11,30] white lines have been observed in a large number of substances. Although the origin of the strong absorption has not been analyzed in detail, it is generally believed[17,23] to be associated with an atomic like electric-dipole-allowed transition from an inner shell to an unoccupied level with a high density of states in the vicinity of the absorbing atom. In this regard, the white line also depends on the chemical bonding because Cu in metal or Cu_2O does not have a white line[19] while W in WO_3 exhibits a broader white line than the one in metallic W.[14]

In this paper, we present some accurate measurements from two separate experiments on the L-edge absorption spectrum of tantalum ($Z = 73$). We are mainly concerned with the Kossel structure for the L_{III} and L_{II} edges with similar white lines, and the L_I edge without a while line. Using the least-squares method, we have fitted the L_{III} white line with two types of profiles, namely the Lorentzian shape[31,32] and the Breit-Wigner-Fano form.[33,34] Although the white lines have not previously been analyzed in such detail, the idea is by no means original. In 1949 Cauchois and Mott[17] suggested that the white line was similar to the resonance in slow-neutron scattering,[33] stating that they hoped to publish a more detailed mathematical investigation on this subject which, to our knowledge, has not been done so far. In the

following, we will first describe the experimental results and then discuss the profile analyses. A preliminary report of our results has been given elsewhere.[35]

II. RESULTS

The Ta L-edge absorption spectrum at liquid-nitrogen temperature has been measured with two x-ray spectrometers. The first one, which has been described by Lytle *et al.*[7,36] consists of a conventional bremsstrahlung source and a LiF (200) single crystal ($2d = 4.0267$ Å). The effective angular divergence of the x-ray beam is $\Delta\theta = 0.025°$ which gives rise to a moderate resolution.[37] The second spectrometer makes use of the synchrotron source at Stanford[11,38] with a channel-cut Si (220) crystal ($2d = 3.8397$ Å). Since the intense source is at 20 m from the slit, a slit width of 1 mm limits the $\Delta\theta$ to 0.00286°, which yields a high resolution ($\Delta E \leq 2$ eV), comparable to a double-crystal spectrometer. The instrumental profile has not been studied, although some theoretical estimates for the multiple Bragg reflection monochromators are available.[39] According to a handbook,[38] the spatial distribution of electrons in the synchrotron source is approximately Gaussian.

Figure 1 shows the x-ray absorption spectrum at the L edges of Ta obtained with the synchrotron source. The linear absorption coefficient μ, multiplied by the thickness of the foil X ($\sim 2.5 \times 10^{-4}$ cm) is plotted against the photon energy relative to the Ta L_{III}-edge inflection point which is set at 9881.1 eV from a standard value listed by Bearden and Burr.[40] Note that taking the inflection point, where $d^2\mu/dE^2 = 0$, as the Fermi energy E_F is only valid when the unoccupied states are uniformly distributed.[41] But in the absence of a better alternative, the inflection point has been generally taken as the position of the absorption edge and identified with E_F.[1,14] For the synchrotron experiments two ionization chambers measure the x-ray intensities before and after passing through the sample. The logarithm of the ratio is plotted directly, which is the reason that the ordinate exhibits negative values.

The two sharp peaks at the L_{III} and L_{II} edges are the white-lines. These are due to transitions from the $2p_{3/2}$ and $2p_{1/2}$ levels, with statistical weights of 4 and 2, respectively, to the vacant $5d$ levels.[12] The L_I edge which does not exhibit a white line is due to transitions from the $2s$ level to higher-lying $6p$ orbitals. The spectrum shown in Fig. 1 may be compared, say, with the L-edge absorption of gold,[36,42] whose $5d$ levels are all filled, and consequently does not exhibit a white line. For the case of Pt,[14,16,27,28] there is only one d vacancy (presumably $J = 5/2$) available such

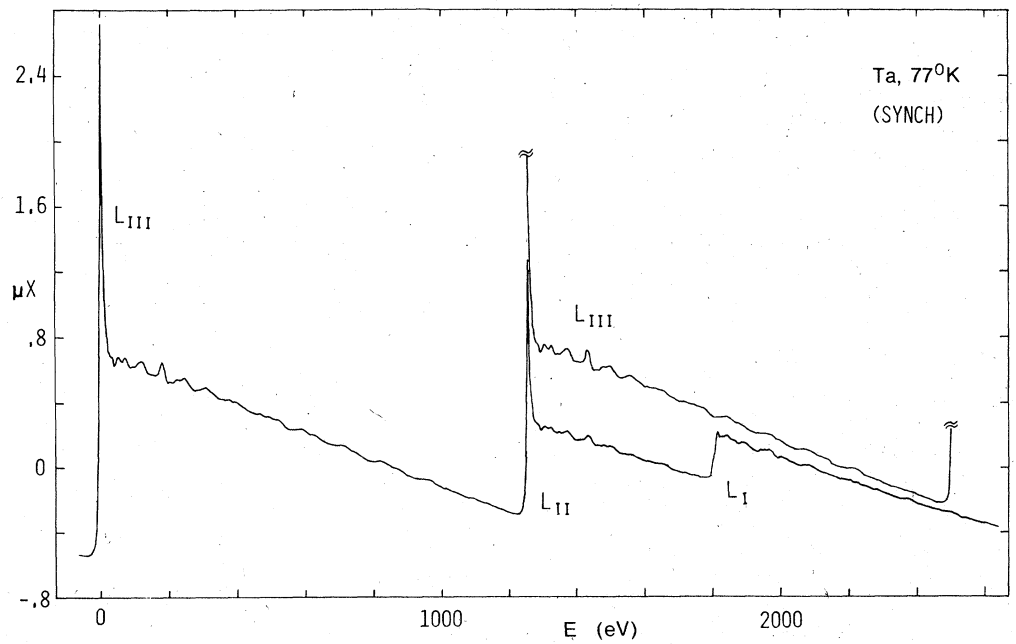

FIG. 1. X-ray absorption spectrum at the L edges of tantalum measured from a synchrotron source. The sharp spikes at the L_{II} and L_{III} edges are called white lines for a historical reason. The x-ray energy scale is plotted relative to the L_{III} edge which occurs at 9881.1 eV. For comparison, the L_{III} absorption fine structure is replotted above the L_{II} and L_I edges.

that the L_{III} edge has a white line but L_{II} and L_I do not, because their transitions to $5d_{5/2}$ would be quadrupolar. Note that for x-ray transitions involving inner-shell electrons, the electric-dipole-forbidden transitions are at least 10^3 weaker than the allowed ones.[43]

For energies higher than about 50 eV above each edge, the variation in μ is known as the Kronig structure or EXAFS which contains structural information about the absorbing atoms.[5-11] We will not go into details about EXAFS except to say that the *Ta* L_{III} EXAFS has about twice the amplitude of the L_{II}, and that the L_{II} EXAFS may extend well beyond the L_I edge (see Fig. 1). Thus the Kossell and EXAFS structure at L_I may be modulated by the Kronig structure from L_{II}.

We have also made measurements with the bremsstrahlung source. The overall appearance of the Ta L-edge spectrum is similar to that shown in Fig. 1 except that the structure is less pronounced. The instrument has been calibrated to an accuracy of about 1 part in 10^4 using several L-emission lines of W.[44] The Ta L_{III} edge was measured to be 9880.3 ($\pm$0.6) eV, where the uncertainty was assumed to equal one-half the step size in energy.

In Table I we summarize the measured edge positions, the energy resolution ΔE,[37] and the step sizes from the two experiments. The standard listed values[40] for the Ta L edges are also included in Table I for comparison. For the synchrotron source, an absolute calibration on the x-ray wavelength has not been made. Yet, the separation between the L_{II} and L_{III} edges is in excellent agreement with that calculated from the listed values. Note that the atomic energy levels[40] have been evaluated mainly from x-ray emission lines and photoelectron spectroscopy. Absorption edge measurements in the past were less accurate. With the advent of a synchrotron source which is 5×10^4 times more intense than a conventional x-ray source,[11,30] the absorption spectra, once calibrated, should provide an accuracy at least comparable to the other two methods.

Figure 2 shows the Ta L_{III} and L_{II} Kossel structure from the two experiments plotted in an expanded scale. The inflection point of each curve is lined up at zero of the energy scale. We see that the L_{II} line shape, after multiplication by a factor of ~2, is essentially identical to the L_{III}. Thus the high-resolution L_{III} white line alone is the subject for profile analyses. Comparing the two sets of data, it is obvious that the instrumental effects may shift the peak position and distort the line shape. Nevertheless, the separation between the L_{III} and L_{II} edges for each experiment remains about the same (see Table I).

Figure 3 shows the Ta L_I Kossel structure in an expanded plot. Data points from the synchrotron experiment, which is of a much higher resolution than any of the previous work,[12,15,23] exhibit an early inflection point and a small peak. These characteristics are smeared out by the finite resolution in the data from the bremsstrahlung source. Thus these new features now resolved illustrate the reason for a larger discrepancy in the edge position for L_I (Table I).

III. ANALYSIS

X-ray absorption may be considered as an electronic transition from a filled orbital to an unfilled orbital. The band structure of neutral Ta atoms in the solid state (without a core hole) has been calculated by Mattheiss[45] and by Petroff and Viswanathan.[46] In both sets of calculations, a sharp peak of the vacant d band is found. According to the former,[45] a d band of width ~0.5 eV at half maximum would be peaked at 4.6 eV above E_F, whereas the latter[46] would yield a d band of ~0.8 eV width and located at 3.0 eV above E_F. The Ta $2p_{3/2}$ level width may be estimated to be about 3.5 $\pm$ 0.5 eV from an extrapolation of the $2p_{3/2}$

TABLE I. Ta L edges, a comparison of the measured absorption-edge inflection points with the standard listed values (in units of eV).

	Measured, this work						Listed[d]	
	Bremsstrahlung[a]		Synchrotron[b]		Step[c]	Recommended		Absorption,
Edge	Inflection	ΔE	Inflection	ΔE	size	value	Photoelectron	Bearden
L_{III}	9880.3	13.1	9881.1	1.43	1.2	9881.1(±0.3)	9880.3	9877.7
L_{II}	11135.0	16.9	11135.9	1.84	1.5	11136.1(±0.3)	11136.1	11132.0
L_I	11680.5	18.7	11677.9 11691.4	2.03	1.8	11681.5(±0.3)	11680.2	11682.0

[a] With a LiF(200) single crystal. The energy scale is calibrated with W L lines.
[b] With a channel-cut Si(220) crystal. The energy scale is fixed by setting L_{III} to the recommended value.
[c] For both sets of experiments. The uncertainty of the measurement is about one-half of the step size.
[d] From Bearden and Burr, Ref. 40.

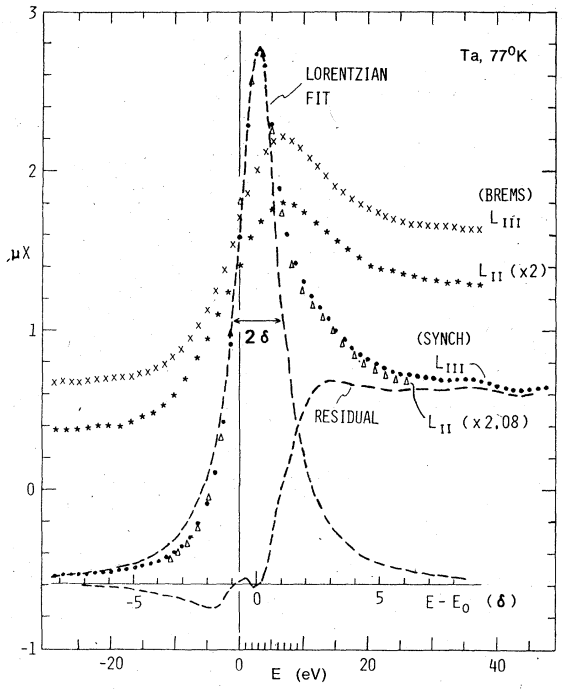

FIG. 2. Ta white lines in an expanded plot with all the edges lined up at their respective inflection points as the zero of the energy scale. The data points are as follows: from the synchrotron source ●, L_{III}; △, L_{II}; from the bremsstrahlung source ×, L_{III}; *, L_{II}. The L_{II} data have been multiplied by a factor of ~2 and shifted vertically to show the general similarity with the L_{III} edge. The former L_{III} data are fitted with a Lorentzian shaped peak and a residual part in dashed curves.

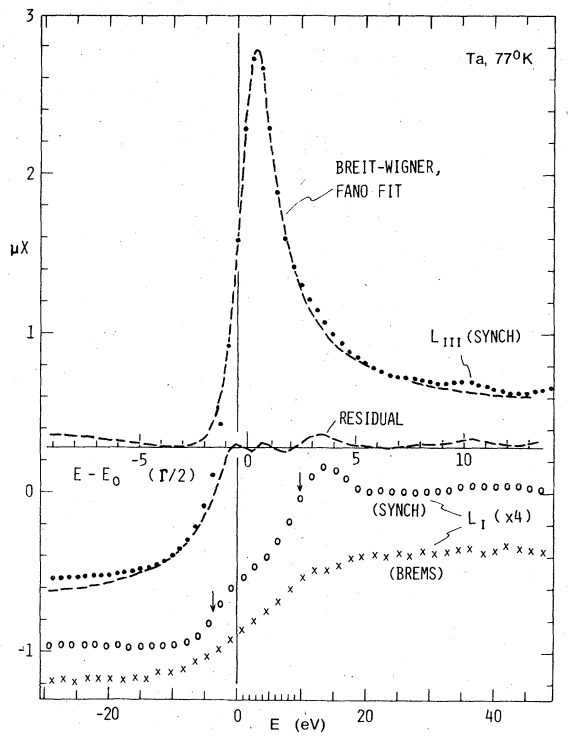

FIG. 3. Ta L_{III} edge (● synchrotron data) as fitted with a Breit-Wigner-Fano-type line shape and a residual part in dashed curves. The latter is compared with the L_I edges (×4): × from the bremsstrahlung source, with the inflection point lined up at $E=0$; and o from the synchrotron source, lined up with the previous data but with the two inflection points (designated by arrows) occurring below and above zero.

widths for Au, Pt, and W.[14] In Fig. 2 and 3, the L_{III} white line (data points from the synchrotron experiment, represented by dots) exhibits an apparent width of ~8 eV. This is consistent with the combined widths of the $2p_{3/2}$ level, the d-band density-of-states peak, and the instrument resolution of 1.4 eV. However, the line shape bears no resemblance to the calculated density of states.

In attempting to learn more about the white lines, we have fitted the Ta-L_{III} data with two established functional forms, as shown in Fig. 2 and 3. Note that there are many possible methods of parametrizing a line shape. An excellent review on absorption-line profiles in connection with the scattering theory has been given by Shore.[47] The present experimental line shape is probably very close to the "true" line shape, because the instrumental width is less than 20% of the observed width. In the following we will neglect the effect of this instrumental broadening. *No prior assumption is made concerning the background at the edge. After subtraction of a resonance profile from the experimental data, the residual part is identified as the background.*

A. Lorentzian fit

From the theory of atomic spectra,[48,49] if the excited states follow an exponential decay in the absence of external interference, then the natural line profile may be expressed by a Lorentzian form:

$$L(E) = a_1/[1 + (E - E_0)^2/\delta^2] + b_1, \quad (1)$$

where E is the energy, E_0 is the peak position, δ is the half width at half maximum, and a_1 and b_1 are constants. An excellent example of using the Lorentzian form to reduce the x-ray absorption line shape has been demonstrated by Parratt and his co-workers.[31,32] They showed that the K-edge absorption spectrum of gaseous argon ($Z=18$) could be resolved into a series of Lorentzian profiles decreasing in strength to higher energy as in a Rydberg series for potassium ($Z=19$).

In the present case, since the L_{III} white line is

asymmetric whereas the Lorentzian is even in E, we have chosen to fit the steeper side of the peak by calculating L at several strategic E positions as a function of the parameters E_0, δ, a_1, and b_1. By minimizing the sum of the square deviations $\sum(\mu X - L)^2$, the best fit is found[50] with the following set: $E_0 = 2.675$ eV, $\delta = 3.827$ eV, $a_1 = 3.38$, and $b_1 = -0.59$. Near the optimum, a 1% change in δ can be compensated by a 1.5% change in E_0, which is measured with respect to the edge inflection point. The Lorentzian fit and a residual part are plotted in dashed curves in Fig. 2. A reduced energy scale $(E - E_0)$ in units of δ is also given. In the residual part, a small peak near $E = E_0$ is artificial.

In Fig. 2 the Lorentzian fit can not be considered successful because the L_{III} white line is asymmetric to begin with.[49] Furthermore, unlike the argon absorption spectrum,[31,32] a second Lorentzian peak can not be resolved from the residue part. In the resonance absorption to the Rydberg series which converges to the Ta $5d^36s^2\eta d$ continua, it is possible that the absorption widths may be comparable to or broader than the separation between levels. Also, as discussed by Parratt,[51] the connection between the residual part and the limit for the Rydberg series is not at all clear for a solid.

B. Breit-Wigner-Fano fit

The Breit-Wigner formula[33] was originally used to account for the resonance capture of slow neutrons by certain nuclei. In 1961 Fano[34] rederived the formula when studying the effects of configuration interaction in the electron-impact excitation of autoionizing states in helium. The formula is given by

$$F(E) = a_2(q + \epsilon)^2/(1 + \epsilon^2) + b_2 , \qquad (2)$$

with $\epsilon = 2(E - E_0)/\Gamma$. Where ϵ is the reduced energy (in units of one half the width Γ) measured from the resonance position E_0 (not the peak), q is a line-shape parameter, and a_2 and b_2 are constants. Equation (2) has been very useful in analyzing the cross sections for many scattering processes which include photoabsorption,[52-54] e-atom,[55] e-molecule,[56] atom-molecule,[57,58] surface-state resonance in low-energy-electron diffraction (LEED),[59,60] and e-energy loss from solids.[61] It is perhaps sufficient to say that the Breit-Wigner-Fano formula is applicable whenever two (or more) processes of different energy dependence contribute to the same complex scattering amplitude. The experimental cross section, which is proportional to the product of the scattering amplitude and its complex conjugate, therefore depends on an interference effect of the two contributions.

In fitting the Ta L_{III} white line, we have selected four points from the low-energy side of the peak and six points from the high-energy side. By minimizing $\sum(\mu X - F)^2$ as a function of the parameters,[50] it is possible to find the condition for the best fit as follows: $q = 3.30$, $\Gamma = 6.74$ eV, $E_0 = 1.54$ eV (measured from the inflection point), $a_2 = 0.21$, and $b_2 = 0.28$. Near the optimum, the fitting is not sensitive to the parameters in that for $\Delta q = \pm 0.1$ and $\Delta\Gamma = \pm 0.2$ eV, it is possible to adjust ΔE_0 within a range of ± 0.05 eV and varying the constants slightly to compensate for the changes. The Breit-Wigner-Fano fit and a residual part are plotted in Fig. 3 in dashed curves. A reduced energy scale $\epsilon = E - E_0$ in units of $\Gamma/2$ is also given. In the residual part, the small saw-toothed structure near $\epsilon = 0$ is an artifact of the curve fitting, but the two humps located at 3.4 and 10.3 are real. The peak position occurs at $\epsilon = 1/q$, or 2.56 eV from the inflection point.

IV. DISCUSSIONS

A comparison between Figs. 3 and 2 shows that the Breit-Wigner-Fano form provides a better fit to the asymmetric line shape. Furthermore, it appears that the white line may be separated into a resonance part and a background residual part which is a stepped plateau. Note that in the absence of a large resonance peak, the L_I edge of Ta,[12,15] or the L edges of Au,[27,36,42] may be approximated by a simple step. Since the step at the Ta L_I edge is about 1/4 that of the L_{III} (see Fig. 1), we have plotted in Fig. 3 the Kossel structure from the two measurements. It is gratifying (or fortuitous) to find that the two small humps in the L_{III} residual occur at about the same relative positions as the small peaks in the L_I data from the synchrotron source.

For the white line as fitted in Fig. 3, the resonance position E_0 and the peak are measured to be 1.54 and 2.56 ± 0.05 eV, respectively, above E_F. The important observation is that both values are smaller than the calculated positions[45,46] of the unfilled d-band peak above E_F. Note that the d-band width and positions are less certain in the presence of a core hole. Thus the observed discrepancy may be regarded as evidence for band lowering under the influence of the inner-shell vacancy during the lifetime[3] of the resonance ($\tau = h/\Gamma \sim 10^{-16}$ sec). In a way this is analogous to the β decay of a nucleus in which the nuclear charge is suddenly increased by one unit. Qualitatively, the vacant d band would move closer to the Fermi energy as the atomic number increases.[62]

Although the ordinary band-structure calculation may fail to exactly describe x-ray absorption, it is adequate in interpreting x-ray isochromat experiments[63-65] where no core level is involved, e.g., compare the L_{III}-edge absorption line shapes of the 5*d* metals Ta, Ir, Pt, and Au,[27] with isochromats of the same elements.[64] The two kinds of experiments are similar in the determination of *d*-band occupancy, but they are different in detail.

The application of the Fano or Breit-Wigner-type formula does not necessarily imply that the physical mechanism is dominated by configuration interaction,[34] although the absorption from an inner shell is always autoionizing. If the L_{III} (or L_{II}) absorption is considered as an electric-dipole transition from the initial state $2p^6(MN\ 5s^25p^6)5d^36s^2\ ^4F$ to discrete final states of the types $2p^5(MN5s^25p^6)5d^46s^2$, then each possible term of the latter may interact with a number of continuum states of the type $(KLMN\ 5s^25p^6)5d^26s^2\eta p$ and $(KLMN\ 5s^25p^6)5d^26s^2\eta f$. The possible combinations will be much larger if electrons from the closed shells may also be excited.

The helium $2s2p\ ^1P^0$ autoionizing state[34,52,53] for which the resonance formula was first derived has a lifetime τ of about 1.7×10^{-14} sec, which is much longer than that of the Ta white line. Yet, it is interesting to find that the ratio E_0/Γ in both cases turns out to be about the same ($\sim1.5\times10^3$). Whether this is a coincidence or something more basic to the resonances may deserve further consideration. For the He $2s2p\ ^1P^0$ state, the resonance parameter q turns out to be -1.8 and -2.8, respectively, from the electron impact[34] and photoabsorption[52,53] experiments. In view of the results shown in Fig. 2, it is our opinion that the difference is probably due to instrumental resolution rather than due to the different means of excitation.[3] In principle, one should be able to extract more physical meaning from the resonance parameters; however, in practice this has not been very successful.[3,34,53]

Recently, Dietz *et al.*[61] analyzed the electron-impact line shape for the $3p\rightarrow3d$ excitation in Ni metal using the Fano-type formula. They interpreted the results as entirely due to configuration interaction, and not related to the many-body effects.[66] In contrast, Mahan[67] has studied the soft-x-ray absorption spectra of several simple metals in terms of collective excitation effects with moderate success. It thus seems apparent that further effort is needed for a more quantitative understanding of the x-ray absorption edges in solids.

To summarize, the x-ray absorption spectrum of the Ta *L* edges has been measured in two experiments. The results are found to be consistent. The high-resolution measurements from the synchrotron source, once calibrated with respect to some prominent features such as the white lines, may give rise to accurate determination of atomic energy levels. The observed L_{III} white line exhibits a skewed line shape which does not bear resemblance to the calculated unfilled density of states. This is expected because the effect of a short-lived core hole has not been included in the existing band-structure calculations for Ta. The L_{III} line shape was first fitted by a Lorentz profile. However, the fit for Ta was less successful compared with the case for gaseous Ar,[31,32] in that a sequence of discrete states like a Rydberg series converging to a limit could not be resolved. Inspired by a statement made by Cauchois and Mott,[17] we have also analyzed the L_{III} line shape in terms of the Breit-Wigner- or Fano-type formula for resonance absorption. Although the latter fit appears to be better, it is by no means exclusive. Besides, the physical meanings of the parameters are not well understood, especially if unresolved overlapping resonances[68] may be involved.

We conclude that the present understanding of the effect is ambiguous, and we wish to stimulate theoretical interest in the problem.

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