PHYSICAL REVIEW B VOLUME 15, NUMBER 2 15 JANUARY 1977

White lines in x-ray absorption*

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(Received 13 August 1976)

A quantitative discussion of the white line at the L_3 edge of platinum and its absence at the L_2 edge in x-ray absorption is presented. The predominance of $d_{5/2}$ character in the hole in the atomic $5d$ shell of Pt is shown to persist in the unoccupied portion of the d band of the metal. The total weight in the L_3-edge white line is calculated and found consistent with the experimental value. A brief presentation of some experimental results is given including some suggestion of the range of validity of the sudden approximation in x-ray absorption.

I. INTRODUCTION

One of the most spectacular features of x-ray absorption is the "white line" visible in many K- and L-edge spectra. The "white line" is a large peak in the absorption coefficient occurring near absorption edges. At the time when this phenomenon was first observed x rays were detected photographically and the large absorption peak appeared as an unexposed white line on the negative. Many experimental examples of "white lines" have been found.[1] The L-edge results are richer in possibilities than K-edge results because there are three L edges. In cases where they occur the white lines are usually present on both the L_3 and L_2 edges simultaneously and not the L_1 edge, or vice versa. Usually the former case occurs, but Te is an example of the rarer latter situation[2] as shown in Fig. 1. The more common situation is illustrated by Ta, which has white lines at both the L_2 and L_3 edges but none at the L_1 edge. Figure 2 shows the white line at the L_3 edge.[3]

The cause of the "white lines" has been qualitatively understood as due to a high density of final states or due to exciton effects.[4,5] The difference between the L_1 and the $L_{2,3}$ edges comes about because L_1 initiates from the $2s$ state while $L_{2,3}$ initiate from the $2p$ state. These thus probe the density of final states with different symmetries. The L_1 edge (as does the K edge) probes the p-symmetric portion of the density of final states, while the $L_{2,3}$ edges probe the s- and d-symmetric portions. Since one normally expects the s-symmetric portion of the density of states to be small and spread out in energy, one does not expect white lines from this symmetry. However, the d-symmetric portion of the density of states can become large and narrow and is thus a likely candidate to produce white lines. This is verified by experiments[1,2,6-10] which indicate that white lines in the $L_{2,3}$ edge are limited to metals where unoccupied d states occur at the Fermi energy.

In a solid the symmetry of the final states cannot be described straightforwardly in terms of s, p, d, etc., symmetry because the potential around each atom is not spherically symmetric, and because of band effects. However, the initial state (e.g., an L state) is confined to a small central region in the atom, in which these deviations from spherical symmetry are negligible, so that this state may be taken as an eigenstate of angular momentum, as in the atom. By the selection rules for electric dipole radiation the transition therefore probes that part of the final-state wave function which has the appropriate symmetry.

The white lines in K- and L_1-edge spectra must be caused by p-symmetric final states. Normally the p-symmetric final density of states is small and spread over a wide energy range as is the case for s symmetry. However, under the right conditions in a semiconductor or insulating crystal excitons can be formed in the p-symmetric final states giving the narrow energy width and thus high density of states to produce a white line. The positively charged core hole produced when an x ray is absorbed may remain sufficiently unshielded in a semiconductor or insulator as to bind the p state and produce exciton levels. Transitions to these exciton levels produce the white lines as illustrated[3] in Figs. 3 and 4 for Ge and Se, respectively. Both the Ge and Se white lines are superpositions of several Rydberg-like lines. The lines are somewhat narrower in Se. The white line in Te of Fig. 1 is not so clearly caused by excitons and may be some intermediate case where the p state is almost bound. The white lines[2] in the L_1 edge of Sb, Sn, and In are distinguishable from exciton lines and are caused by high density of p states.

The line shape may permit a distinction to be made between exciton white lines and those caused by a high density of states imbedded in a continuum. An exciton or bound state will produce an approximately Lorentzian peak shape, while a high density of states imbedded in a continuum

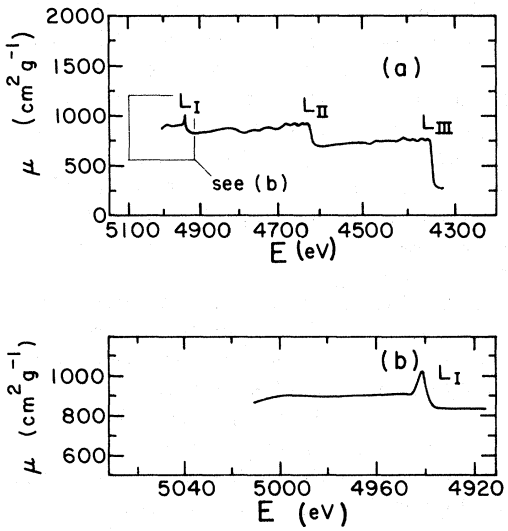

FIG. 1. (a) L-edge absorption for Te as measured by Ref. 2. The L_I-edge region is shown enlarged in (b) with its white line.

produces an absorption peak which may be skewed.[11]

This qualitative understanding has not been matched by quantitative calculations. There have been only a limited number of attempts to quantitatively calculate the characteristic of white lines. A calculation of the L_3-edge white line in Ni metal has given a semiquantitative agreement with its shape,[12] but no magnitude comparison was

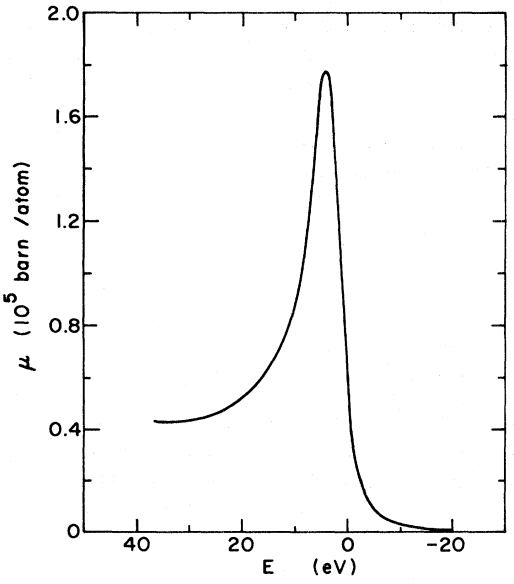

FIG. 2. L_3 edge of Ta metal illustrating the large white line. The smooth background is subtracted showing only the discontinuity at the edge.

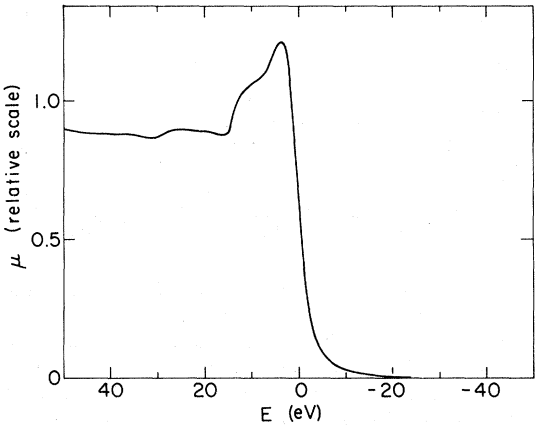

FIG. 3. Near-edge structure at the K edge of Ge illustrating the exciton structure giving rise to the white line. The smooth background is subtracted showing only the discontinuity at the edge.

made—the calculation being normalized to the experimental value. This calculation included band effects but neglected many-body effects and the core hole-electron interactions. A similar calculation[13] gives poor agreement for the shape of the white line at the $M_{2,3}$ edge of Ni. One of the many-body effects that cannot be neglected at the low x-ray energies of the $M_{2,3}$ edge[14] is the configurational mixing between the continuum of transitions which are degenerate in energy with the transitions from the discrete core state.[11] Calculations including this effect appear to give agreement with electron-energy-loss experiments at $M_{2,3}$-edge energies[15] but the same calculations do not explain the x-ray absorption data[16] for the same edge. Perhaps the clearest case to illustrate that our understanding of white lines is not

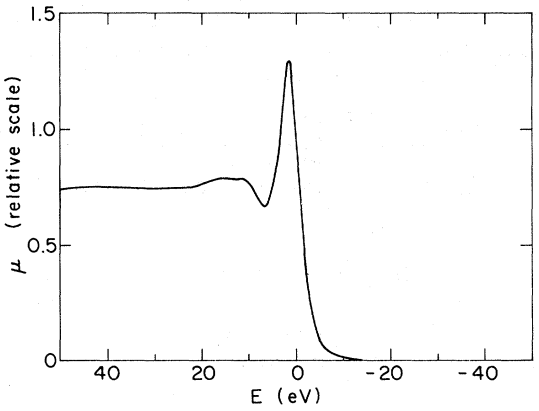

FIG. 4. Near-edge structure at the K edge of Se illustrating the exciton structure giving rise to the white line. The smooth background is subtracted showing only the discontinuity at the edge.

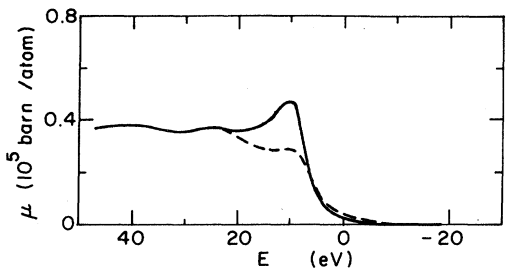

FIG. 5. L_2 (dashed) and L_3 (solid) edges of Pt metal. The two edges are shifted in energy so that they line up and the L_2 edge is multiplied by a factor 2.22 so as to coincide with the L_3 edge 40 eV past the edge. Note that only the L_3 edge has a significant white line. The smooth background is subtracted showing only the discontinuity at the edge.

complete is that of Ti. The L_3 x-ray absorption edge of Ti shows no white line[17] even though Ti is a transition metal with a high density of unoccupied d states.

There is a need for added quantitative studies of white lines to help elucidate the matter further. Not only theoretical studies are needed but experimental ones also. The measurements of white lines are characterized by an almost complete lack of reliable quantitative studies. The experimental problem is difficult because of the large change in intensity of transmitted radiation in passing through the white line. This requires an experimental detector that has a large dynamic range of linearity. Photographic film, for example, has difficulty fulfilling this requirement.

Platinum metal is a particularly favorable case to study theoretically because of its experimentally striking properties.[1,7,8,10] The L_1 edge does not have a white line, as is usual for a transition metal, but, what is unusual, the L_2 edge also does not show a significant white line, though the L_3 edge does, as shown[3] in Fig. 5. Mott[4] first suggested that the difference between the L_2 and L_3 edge is caused by spin-orbit effects. The only unoccupied d level in the Pt *atom* is the $d_{5/2}$ state. Only the L_3 edge makes transitions to such a final state, since it originates from a $p_{3/2}$ state. The L_2 edge, originating from a $p_{1/2}$ state, can make transitions only to $d_{3/2}$ and s states. In the metallic form the lack of a white line at L_2 and its presence at L_3 can be understood by assuming that the holes in the d band retain the $d_{5/2}$ character.

To verify this mechanism quantitatively one must calculate various features: (a) One point is to determine how, as Pt atoms condense into the metallic form, the band broadening of the atomic Pt levels will mix the $d_{3/2}$ and $d_{5/2}$ character in the unoccupied portion of the d-band; (b) another is to estimate the oscillator strength of the $2p_{3/2}$ to $5d_{5/2}$ transition to compare with experiment; (c) a third is to include the many-body effects that accompany the interaction between the core hole and the photoelectron in the presence of the conduction electrons.

In Sec. II of this paper we discuss point (a) in the tight-binding approximation. The oscillator strength of point (b) is calculated for an isolated atom in Sec. III. The complicated effects in point (c) are discussed in Sec. IV on only a qualitative basis. Section V consists of a discussion and comparison with experiment, while Sec. VI consists of a summary and conclusion.

II. SPIN-ORBIT MIXING IN BANDS

In this section we treat the tight-binding approximation of d states including spin-orbit interactions. The ratio of $d_{5/2}$ to $d_{3/2}$ character near the top of the band is ascertained for parameters appropriate for Pt metal.

The tight-binding approximation for the $5d$ band assumes an electronic wave function of the Bloch form:

$$\psi_k(\vec{r}) = \sum_n e^{i\vec{k}\cdot\vec{a}_n} \sum_{m_s}\sum_{m_l} b_{m_s m_l} \phi_{m_l}(|\vec{r}-\vec{a}_n|)\,|\tfrac{1}{2} m_s\rangle\,, \tag{1}$$

where $\vec{a}_n$ is the position of atom at the nth lattice site,

$$\phi_{m_l}(r) = R_5(r)\, Y_{2m_l}(\theta,\phi)\,, \tag{2}$$

$R_5(r)$ is the Herman-Skillman atomic radial function[18] for the $n=5$ d orbitals of platinum, Y_{2m_l} is the angular function for d states with a z component of angular momentum of m_l, and $|\frac{1}{2}m_s\rangle$ is the spin state. The $6s$ states were ignored since, as argued above, the white line is caused by the d states. The Hamiltonian with spin-orbit interaction is

$$H = \frac{p^2}{2m} + \sum U(\vec{r}-\vec{a}_n) + \frac{\hbar^2}{2m^2c^2} \sum_n \left|\frac{1}{\vec{r}-\vec{a}_n}\right| \frac{dU(\vec{r}-\vec{a}_n)}{d|\vec{r}-\vec{a}_n|}\, \vec{l}_n\cdot\vec{s}\,, \tag{3}$$

where $U(\vec{r})$ is the Herman-Skillman atomic potential for platinum, and $\hbar\vec{l}_n$ is the angular momentum operator about the nth atom. $H\psi = E\psi$ gives a 10×10 matrix to diagonalize:

$$\sum_{m_s'}\sum_{m_l'}\left[\sum_n\left(e^{i\vec{k}\cdot\vec{a}_n}\int\phi^*_{m_l}(r)\,U(\vec{r}-\vec{a}_n)\,\phi_{m_l'}(|\vec{r}-\vec{a}_n|)\,d^3r+\int_{m_l}\phi^*(\vec{r})\,U(\vec{r}-\vec{a}_n)\,\phi_{m_l'}(r)\,d^3r\right)\delta_{m_s m_s'}\right.$$
$$\left.+\alpha\langle m_l m_s|\vec{l}\cdot\vec{s}|m_l' m_s'\rangle-(E-E_0)\,\delta_{m_l m_l'}\delta_{m_s m_s'}\right]b_{m_l' s}=0. \quad (4)$$

Here we assume that the $\phi_{m_l}(r)$ are orthonormal, retain only two-center integrals, and consider only nearest neighbors in the sum. Also E_0 is the free-atom energy,

$$\alpha=\int[R_s(r)]^2\,\frac{\hbar^2}{2m^2c^2}\,\frac{1}{r}\,\frac{dU}{dr}\,r^2\,dr \quad (5)$$

and

$$|m_l m_s\rangle\equiv|l=2,m_l\rangle\,|s=\tfrac{1}{2},m_s\rangle\,.$$

The calculation gave a bandwidth of about 30 eV, as against the observed value[19,20] of about 9 eV. This difference no doubt represents the usual inadequacy of the tight-binding model with free-atom wave functions. In order to obtain a more meaningful comparison the bandwidth matrix elements were scaled down to give approximately the observed value.

The diagonalization determines $E-E_0$ and the $b_{m_s m_l}$'s for each band. From these a Fermi energy E_F is determined by requiring 0.30 hole in the d bands to agree with band calculations.[20] For this purpose it was sufficient to use a simple approximation to estimate the density of states at the top of the band. Owing to the cubic symmetry the Brillouin zone divides into 48 equivalent sections. To examine one of these smaller sections ten *evenly* spaced vectors, from the origin to the Brillouin-zone face, were studied. Imagine a small cone enclosing each vector. It was assumed that the properties of the states located on the small disk sliced out of the cone by a plane perpendicular to the axis are reasonably approximated by the state on the cone axis at the center of the disk. In particular, the ratio of $d_{5/2}$ to $d_{3/2}$ should be approximately the same. It was also assumed that the states enclosed by these ten cones give a good representation of the entire region. Since each area is equally sampled (evenly spaced vectors) and neighboring vectors are similar, this assumption should be sound. E_F was determined by finding the energy above which 0.15 of the volume was enclosed by the 10 cones. Since the top band is doubly degenerate this leaves the desired 0.30 hole.

The ratio of $d_{5/2}$ to $d_{3/2}$ is determined by using the values along the cone axis and weighting by the size of the disk at that point. The result of the calculation is a ratio of 14 to 1. Admittedly this is a crude calculation but the end result is, fortunately, quite insensitive to reasonable variations. For example, leaving an entire hole instead of 0.30 of a hole gives a ratio of about 12.5 to 1 in place of 14 to 1. Considering that we cannot claim any better accuracy for the tight-binding approximation, this difference is unimportant. This result indicates that the band broadening does not substantially mix $d_{5/2}$ and $d_{3/2}$ states in the unoccupied part of the d band of platinum.

III. ABSORPTION CONTRIBUTION OF THE WHITE LINE

In this section we estimate the contribution to the absorption of the $2p_{3/2}\rightarrow 5d_{5/2}$ transition in Pt atoms.

The total absorption A contributed by this transition is

$$A\equiv\int\mu(E)\,dE=\frac{2N_0\pi^2e^2\hbar}{mc}\bar{F}_{fi}\,n_h\,. \quad (6)$$

μ is the absorption coefficient defined by $I/I_0=e^{-\mu x}$, I is the intensity transmitted through a sample of thickness x with incident intensity I_0, m is the free electron mass, N_0 is the number of Pt atoms per unit volume, n_h is the number of d-band holes, and F_{fi} is the oscillator strength given by

$$F_{fi}\equiv(2m/\hbar)\,\omega_{fi}|\langle f|z|i\rangle|^2\,. \quad (7)$$

Here $|i\rangle$ is a $2p_{3/2}$ state for a particular m_j as given by the Herman-Skillman wave functions[18] for Pt, $|f\rangle$ is a $5d_{5/2}$ state for a given m_j as given by the Herman-Skillman wave functions for Au. Gold is chosen to approximate the relaxation effects in the excited atom caused by the $2p_{3/2}$ hole. $\bar{F}_{fi}$ is the average of F_{fi} over different m_j values (from $-\frac{3}{2}$ to $\frac{3}{2}$). n_h is obtained from band calculation for Pt metal[20] as 0.30 holes in the $5d$ band. The numerical value found for (6) was

$$A_{\text{calc}}=1.17\times10^4\ \text{cm}^{-1}\text{eV}\,. \quad (6')$$

IV. MANY-BODY EFFECTS

For a Pt *atom* relaxation effects are reasonably accounted for by using Au-atom final states. The form of the final states are clearly accurately accounted for at radii appreciably larger than the L-shell radius, but the important portion of the excited state is that which most strongly over-

laps the initial $2p_{3/2}$ state. This is in the region where the $2p_{3/2}$ state has its largest amplitude and thus in the region where the $2p_{3/2}$ hole cannot be approximated by a positive charge concentrated at the nucleus. However, since the L shell of Pt interacts with a positive charge of the order of 76, incorrectly approximating the charge of one electron would produce an error of less than 2% in our estimate of relaxation.

However, there is another effect which we have neglected which causes a reduction in the coherent part of the absorption. In calculating the dipole matrix element in Eq. (7) only the electron involved in the transition was considered. Since the atom has many electrons, the matrix element in Eq. (7) must also be multiplied by the product of the overlap between the initial and final states of the "passive" electrons. Because of relaxation in the final state this overlap will be less than unity.[21] An estimate for the Pt atom gives a result of 0.8 instead of the value of 1, the result if there were no relaxation. This is estimated by using Au wave functions for the relaxed state, which should be a reasonable approximation since the states which are most changed by relaxation are the outer ones where an L hole is accurately approximated by an increase in nuclear charge of one.

The absorption can be further reduced by the interaction of a single Pt atom with its neighbors and with the conduction electrons.[22] On the other hand, the reduction is compensated for by "shake-off" processes[23] where more than one electron is excited. In fact the oscillator-strength sum rule[24] assures that what is lost from the single-electron excitation is exactly compensated by multiple-electron excitation. The question of interest is where in energy will these multielectron excitations occur. All those multielectron excitations which occur within the width of the white line would add back to what was lost, and, if the experimental data are analyzed to include these excitations, the total measured absorption should agree with the single-particle calculation of Sec. III.

The line shape of the white line is also affected by the fact that the L-shell transition is degenerate in energy with a continuum of transitions. The continuum may cause the white line to become skewed at the high-energy side.[11,25] However, the total oscillator strength in the white line is not changed by this effect, only redistributed over energy. As long as we can determine the total area from the experimental data irrespective of the shape, we can neglect this effect.

A further effect could cause a discrepancy between our calculation and the measurement. When the L-shell hole is produced, the unoccupied d band will be pulled below the Fermi energy in the fully relaxed state. (The fully relaxed Pt atom with an L-shell hole has d states approximating those of Au.) However, if the sudden approximation is valid (as assumed in the calculation of Sec. III) then the unoccupied d band remains unchanged as the L hole is produced and the 0.30 hole remains unoccupied. In the fully relaxed state the d hole becomes filled. Thus the oscillator strength in the white line will depend on whether the sudden approximation or the adiabatic approximation (where the fully relaxed state is appropriate) or some situation in between is valid. Some experimental evidence that such an effect may exist is given by the absorption spectrum of Ni. The L-edge absorption[26] of Ni shows a six times more intense white line relative to the background than does the M edge.[16] Configuration mixing should be greater for the M edge than the L edge because the continuum background is larger relative to the M-shell absorption than is the case at the L shell. Yet calculations including this effect[15] have not given good agreement with the measured absorption results.[16] The lack of a white line[17] at the L_3 edge of Ti is also unexplained in the sudden approximation. These perplexing experimental results may indicate a breakdown of the sudden approximation.

V. DISCUSSION AND COMPARISON WITH EXPERIMENT

The band calculation given here correctly predicts the qualitative results of the predominance of $d_{5/2}$ character in the unoccupied portion of the d band in the Pt, and thus explains the weakness of the white line in the L_2 edge and its presence in the L_3 edge.

The plot in Fig. 5 indicates a small peak in the L_2 absorption of Pt at the energy corresponding to the white line of the L_3 edge. This peak may be a small white line in agreement with the calculations in Sec. II which do show that the L_2 edge has a white line about $\frac{1}{14}$ the size of that of the L_3 edge. However, some fine-structure oscillations (extended x-ray absorption fine structure, EXAFS) are also apparent and that peak could be part of the fine structure. It is clear that depending on how one subtracts off the background due to the fine structure the weight of the white line at the L_2 edge is greatly uncertain from the experiment. For that reason we do not use the experiment to determine the weight of the white line in the L_2 edge but assume the theoretical value for its weight and check the consistency of this assumption by comparison with the value of the white line at the L_3 edge determined from the experi-

mental data.

In this spirit an experimental value for the total absorption in the L_3 white line of Pt can be obtained by subtracting the plot in Fig. 5 of the μ vs. energy for the L_2 edge from that of the L_3 edge after shifting the L_2 edge to coincide with the L_3 edge and normalizing the L_2 edge so that its μ coincides with the L_3 value for energies 30 eV and greater past the edge. The difference in area between these two curves is then multiplied by $1+\frac{1}{14}$ to correct roughly for white-line weight at the L_2 edge as estimated in Sec. II. The experimental value obtained thusly is

$$A_{\text{expt}} = 1.19\times10^{4}\ \text{cm}^{-1}\,\text{eV}. \tag{8}$$

The ratio between the experimental and calculated [Eq. (7′)] values is

$$A_{\text{expt}}/A_{\text{calc}} = 1.02.$$

The agreement is embarrassingly good and such good agreement must be fortuitous. The uncertainties in both the theoretical and experimental values are appreciably larger than 2%. The Herman-Skillman wave functions do not correctly include relativistic effects. Such effects produce about a 15% correction to the energy and thus could cause an appreciable correction to the wave function. The breakdown of the sudden approximation could also affect the absorption.

The many-body overlap effect discussed in Sec. IV decreases the coherent contribution to the white line but this should just be compensated by the multiple-electron excitations as discussed in Sec. IV. We integrated the difference in the L_2 and L_3 edges up to 30 eV past the edges which experimentally included the significant difference between the two edges and thus presumably all of the significant multiple-electron excitations.

VI. SUMMARY AND CONCLUSION

It has been shown in this paper that the $d_{5/2}$ character of the d hole in atomic Pt remains dominant in the metal, being about 14 times greater than the $d_{3/2}$ character.

The calculated weight of the absorption in the white line corresponding to a $2p_{3/2}$ to $5d_{5/2}$ transition is consistent with the experimentally determined value. However, the uncertainty in the theoretical value permits the existence of neglected effects of the order of 10%. The shape of the white line showing a tailing of up to 30 eV past the edge is indicative of multiple-electron excitations and/or interaction with the continuum. However, these effects do not change the total absorption; they only redistribute the absorption in energy producing the tailing at the high-energy side.

The white line of Pt metal thus can be quantitatively understood in terms of transitions to the unoccupied high density of states of the d band.

The experimental results for Ni and Ti do not fit into the present theoretical framework. This discrepancy may indicate a breakdown of the sudden approximation. Since the L-shell energies of Pt are quite a bit larger than those of Ni and Ti we can have some confidence that our assumption of the validity of the sudden approximation is accurate.

ACKNOWLEDGMENTS

One of us (E.A.S.) wishes to express appreciation to Dr. D. E. Sayers and Bruce Bunker for many discussions and help in analyzing the experimental data. The invaluable help of the staff at Stanford Synchrotron Radiation Project in making it possible to take the data is most gratefully appreciated.

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*Research supported in part by NSF Grants Nos. GH41348 and DMR73-07692 AO2 in cooperation with the Stanford Linear Accelerator Center and the Energy Research and Development Administration.

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