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L_3- to L_2-intensity ratios in soft-x-ray valence-band emission spectra of 3*d* transition metals

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The L_3- to L_2-intensity ratios of the valence-band x-ray-emission spectra of 3*d* transition metals are corrected for effects of Coster-Kronig transitions. A quantity R_E is obtained which is the x-ray-emission analog of the "white-line" L_3- to L_2-intensity ratio measured in x-ray absorption. The values of R_E so obtained do not show evidence for a dependence on magnetic moment that is observed in the corresponding intensity ratios in x-ray absorption. A comparison is made between the values of R_E obtained here, and those of a related quantity determined with use of appearance-potential spectroscopy. We find evidence supporting a spin-orbit-splitting model for the L_3- to L_2-intensity ratio of Ni metal in x-ray absorption.

I. INTRODUCTION

Leapman and Grunes measured the "white-line" L_3- to L_2-intensity ratio for the electron-energy-loss spectra (EELS) of 3*d* transition metals (TM) and found a pronounced deviation from the "statistical" (-weight) ratio of 2:1 (expected on the basis of the $2j+1$ degeneracy of the $2p_{3/2}$ and $2p_{1/2}$ initial core states).[1,2] A deviation from the 2:1 statistical ratio is also observed with use of x-ray-absorption near-edge spectroscopy (XANES).[3] In x-ray absorption, the ratio is much less than 2 for light TM's such as titanium, and significantly greater than 2 for the ferromagnetic TM's iron and nickel.[1,2] More recently, Thole and van der Laan have applied atomic calculations to elucidate the above phenomenon; these authors have also carried out an extensive literature review.[4] Thole and van der Laan make a strong case that there is a magnetic-moment effect on the L_3- to L_2-intensity ratio in x-ray absorption. They show that for materials with 3*d* holes all of the same spin sign (Hund's-rule ground state for iron, as an example), the L_3- to L_2-intensity ratio is enhanced. The L_3- to L_2-intensity ratio in x-ray absorption is influenced by a complex array of causes, however, of which magnetic moment is only one example. Thus, Zaanen *et al.* explain the low L_3- to L_2-intensity ratio as observed in light TM's in terms of a model in which exchange between the ejected electron and the 2*p* core hole, as well as partial breakdown of *j*-*j* coupling are important.[5] For late 3*d* TM's, particularly nickel, slight amounts of spin-orbit splitting near the top of the 3*d* band might also affect the L_3- to L_2-intensity ratio, although this point is controversial. Yamaguchi *et al.* state unequivocally that the 3*d*-band spin-orbit splitting for 3*d* TM compounds is too small to have an effect on the XANES spectra.[6] On the other hand, Thole and van der Laan indicate that 3*d*-band spin-orbit splitting may have a significant effect on the XANES spectra of some nickel compounds.[4]

It would be interesting to compare white-line L_3 to L_2-intensity ratios as observed in x-ray absorption for 3*d* TM's with those of a corresponding quantity observed in soft-x-ray valence-band x-ray-emission spectroscopy (SXS). The x-ray-emission spectra of interest here are excited by incident electrons which eject 2*p* core-hole electrons into states of order 10^3 eV above E_F. The great majority of these ejected electrons are excited into states well above the region of spin-down holes associated with ferromagnetic TM's ($\lesssim 1$ eV above E_F), so that the subsequent x-ray-emission event on average has no "memory" of a preferred spin in the ejected electron. For a ferromagnetic material such as iron, therefore, both majority- and minority-spin occupied-state subbands contribute to the SXS spectra and any effect of spin observed in x-ray absorption would be expected to be weaker in the x-ray-emission case.

There has been a stumbling block to date, however, to making a meaningful comparison between x-ray-absorption and -emission L_3- to L_2-intensity ratios. For the x-ray-emission case, there are intense Coster-Kronig transitions which rearrange the primary vacancy distribution so that the number of L_2 core holes is much reduced relative to the number of L_3 core holes. This effect alone results in a very large enhancement of the observed L_3- to L_2-intensity ratio, where the ratio here refers to the ratio of observed x-ray-emission intensities of the $2p_{3/2}\rightarrow 3d$ (L_3) and $2p_{1/2}\rightarrow 3d$ (L_2) transitions. It is possible, however, to correct the SXS data to account for effects of Coster-Kronig transitions, and to extract a quantity R_E, defined as

$$R_E = 2\Gamma_{x3}^{3D}/\Gamma_{x2}^{3d} , \tag{1}$$

where Γ_{x3}^{3d} and Γ_{x2}^{3d} are the contributions to the total width of the L_3 and L_2 core holes, respectively, of x-ray-emission events associated with $2p_{3/2}\rightarrow 3d$ and $2p_{1/2}\rightarrow 3d$ transitions. It is this ratio (R_E) which will be the x-ray-emission quantity here to be compared with the white-line L_3- to L_2-intensity ratio (R_A) observed in x-ray absorption. In the following, a method of extracting R_E from the data will be described, these R_E values will be deduced from appropriate SXS spectra as measured by several authors, and the relationship between R_E and a similar quantity obtained in a total-yield experiment (soft-x-ray appearance-potential spectroscopy, or SXAPS) will be discussed.

II. METHOD OF EXTRACTING R_E FROM SXS INTENSITY RATIOS

Recently, Pease has compared experimental I_{x3}^{3s}/I_{x2}^{3s} ratios to ratios calculated on the basis of different assumptions regarding the values of Γ_2 and Γ_3, where I_{x3}^{3s}, I_{x2}^{3s}, Γ_2, and Γ_3 correspond to the SXS intensity for $2p_{3/2} \rightarrow 3s$ transitions, the intensity for $2p_{1/2} \rightarrow 3s$ transitions, the lifetime width of the L_2 core hole, and the lifetime width of the L_3 core hole, respectively.[7] In that study, the following conclusions were drawn: (1) For the best true lifetimes, one should use theoretically calculated Γ_3 widths,[8] as opposed to experimental widths; the experimental widths contain "non-lifetime" contributions to the broadening. (2) For the best true Γ_2 lifetime widths, one should add to the theoretically calculated Γ_3 widths the experimental difference between the Γ_2 and Γ_3 widths as determined by x-ray-photoemission spectroscopy (XPS). (3) A parabolic fit to the XPS data of Fuggle and Alvorado[9] gives good agreement with the SXS results, if used as described in (1) and (2) above, although the agreement is poor if the Coster-Kronig widths of Nyholm *et al.*[10] are used. A simple extension of the development in Ref. 7 leads to the following expression for R_E:

$$\frac{I_{x3}^{3d}}{I_{x2}^{3d}} \approx \left[2+\frac{\Gamma_2-\Gamma_3}{\Gamma_2}\right]\frac{\Gamma_2}{\Gamma_3}\frac{R_E}{2} . \qquad (2)$$

Then, from measured spectra, obtained under conditions such that self-absorption effects are negligible,[11] and from the core-hole widths, values of R_E are extracted.

The data are taken from three references. For the $2p \rightarrow 3d$ SXS data of Cu, Ni, Co, and Fe, the results of Hanzely and Liefeld[11] are used. For Cr, the data of Fisher[12] is used; for Ti, the results used are those obtained by Fischer and Baun.[13] Careful experimental techniques were used in obtaining these spectra, and most important, self-absorption in the anode was negligible for the spectra used in the present investigation. Omitted from the data set is the Zn spectrum of Hanzely and Liefeld.[11] The SXS spectrum of Zn $2p \rightarrow 3d$ transitions is observed to be by far the narrowest of all these spectra, in agreement with modern calculations of the Zn $3d$-band width;[14] this spectrum is so narrow that the width of the points used in the published graph of the data is a significant fraction of the L_3 width. Also omitted is the SXS spectrum of vanadium $2p \rightarrow 3d$ transitions obtained by Fischer;[15] the high- and low-energy tails of this spectrum flatten out at distinctly different intensity levels, which interferes with one's ability to extract meaningful L_3- to L_2-intensity ratios from the data.

The $2p \rightarrow 3d$ peaks in SXS spectra are distorted by satellite emission lines appearing at the high-energy region of the peaks. These lines can be an obstacle to measuring the true L_3- to L_2-intensity ratio. At the outset, however, the point is made that the method of comparing $2p \rightarrow 3d$ with $2p \rightarrow 3s$ peaks to obtain R_E is "robust" in the sense that significant trends can be obtained merely by inspection of the data and do not depend on fine details of the data analysis. Figure 1 shows a comparison of the $2p \rightarrow 3s$ and $2p \rightarrow 3d$ SXS spectra for Cu and Fe. For Cu, the L_3- to L_2-intensity ratio appears to be about the same for both types of spectra, showing that the Cu R_E is close to the statistical ratio of 2. For Fe, the $2p \rightarrow 3s$ L_3- to L_2-intensity ratio is much enhanced relative to that for Cu; this enhancement is due to the much larger Coster-Kronig width in Fe and is quantitatively explained in the article by Pease on $2p \rightarrow 3s$ x-ray spectra.[7] Since the $2p \rightarrow 3d$ L_3- to L_2-intensity ratio in Fe is much smaller than the $2p \rightarrow 3s$ L_3- to L_2-intensity ratio, R_E for Fe is significantly *less* than the statistical value of 2. The corresponding absorption ratio R_A for iron exceeds 3,[2] and one therefore immediately deduces from the raw data alone that R_A greatly exceeds R_E for ferromagnetic iron.

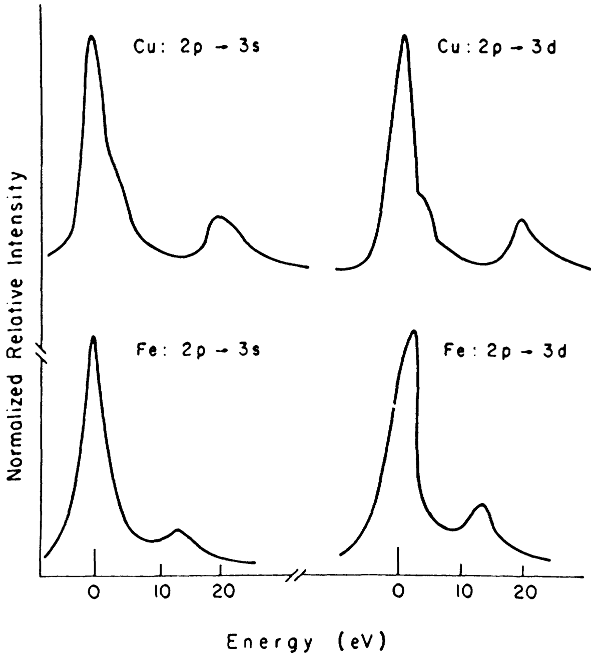

FIG. 1. Comparison of $2p \rightarrow 3s$ and $2p \rightarrow 3d$ SXS spectra for Cu and Fe.

III. METHODS FOR DETERMINING INTENSITY RATIOS

The peaks in the SXS spectrum are distorted on the high-energy side by the effects of satellite emission. As discussed below, the resulting shape of the L_2-intensity peak is different from the shape of the L_3-intensity peak. Therefore, one cannot use those deconvolution procedures used to obtain ratios in EELS (Ref. 2) or SXAPS,[16,17] which depend on the L_3 and L_2 peaks being essentially of the same form.

In order to determine intensity ratio from the data and then to extract R_E values using expression (2), an approach is used in which upper and lower limits are placed on the R_E values. The method used takes the following characteristics of the data into account:

(1) For these spectra, satellite emission skews the peak shapes to high energies. For elements Cr through Ni, the L_2 peak becomes progressively broader in the satellite region relative to the L_3 peak as the 3*d* band becomes filled. The L_2-peak width is also enhanced relative to that of the L_3 peak in Cu.

(2) For elements such as Co and Ni, for which the L_2-peak distortion is most pronounced, the L_3 and L_2 peaks are more widely separated, and overlap effects are smallest.

(3) The titanium SXS spectrum is different in character from the other SXS spectra. Extra fine structure appears so that there is no single, well-defined minimum point between peaks. The titanium SXS spectrum must be treated differently than the others and the error bars on the value of the ratio are more crude.

For elements Cr through Cu, a lower bound on the intensity ratio can be obtained simply by choosing the point of minimum intensity between peaks and counting all area corresponding to higher energy than this point as L_2 intensity and all area corresponding to lower energy than the minimum intensity point as L_3 intensity. All of these peaks are skewed to high energy because of satellite distortion, and the L_3 intensity is always much greater than the L_2 intensity. These two factors combine to insure that, if area ratios are determined in the above manner, a larger fraction of the area counted as L_2 is actually L_3 than is the fraction of the area counted as L_3 which is actually L_2. The present author has tested the assumption that a lower limit to the ratio is thus obtained by superposing the well-separated Cu L_3 and L_2 peaks, using artificial, small L_3-L_2 peak separations. An area-ratio measurement with a division point at the intensity minimum always results in a value lower than the actual one for the ratio. For titanium, there are two minima between the L_3 and L_2 peaks. In order to obtain a conservative, lower bound on R_E, the lowest energy minimum, which is actually closer to the L_3 peak than to the L_2 peak, was chosen as the division point for the area measurements.

For elements Cr through Cu, an upper bound to R_E may be obtained with use of either a variant to the area-ratio measurement described previously, or a Lorentzian fit. The method which gives the smallest upper bound for Cu, Ni, and Co, which have well-separated peaks but serious satellite distortions, is a modified area-ratio method.

The modified-area-ratio method depends upon the fact that the high-energy tail of the L_2 peak extends further above the L_2-peak maximum than does the corresponding L_3 tail extend above the L_3-peak maximum. That the L_2 peak should be broader than the L_3 peak is to be expected on the basis of the greater lifetime broadening of the L_2 core hole relative to that of the L_3 core hole; the difference between experimental L_2- and L_3-peak widths is even greater than can be accounted for by lifetime broadening alone, particularly for Ni, and may be related to a greater satellite distortion for the L_2 x-ray-emission spectra.

In the modified-area-ratio method, a region of the high-energy tail above the L_2 peak is defined, with a low-energy cutoff E_0 chosen at energy value ΔE above the L_2-peak maximum, where ΔE is also the energy between the L_3 peak and the minimum between the L_3 and L_2 peaks. This high-energy L_2 tail region is then multiplied by a normalization factor such that the intensity of the L_2 tail at the low-energy cutoff E_0 matches the intensity of the actual spectrum at the minimum between the L_3 and L_2 peaks. The area of this normalized high-energy tail is then subtracted from the area corresponding to energies greater than the minimum point between peaks, and added to the area corresponding to energies less than the minimum point between peaks. The resulting modified-area ratio overcorrects for the extension of the L_3-peak into the L_2-peak region and an upper limit is thus obtained for R_E for three reasons:

(1) The contribution to the intensity at the minimum is assumed to be completely due to L_3, although there must be some L_2 contribution at this point.

(2) No L_2 contribution is counted as occurring for energies less than the minimum, although there must be some L_2 contribution in this region.

(3) The tail counted as an L_3 contribution under the area corresponding to energies greater than the minimum extends to higher energy than does the actual L_3 contribution in this region, since the L_2 tail is used to model the L_3 tail and the L_2 spectrum is broader than the L_3 spectrum.

For iron and chromium, a Lorentzian fit is used instead of the modified-area-ratio method. In the Lorentzian fit, the L_3 and L_2 peaks are given a separation such that the data and the fit match at the low-energy edge of each peak, the L_3 width is chosen to match the data, and the L_2 width is taken to be greater than the L_3 width by an amount equal to the difference between the L_3 and L_2 lifetime broadening. Various R_E values are chosen until the data and the Lorentzian superposition match heights at the L_3 and L_2 peaks. For Fe, a good match of L_3 height, L_2 height, and minimum between peaks is thus obtained, but the high-energy L_2 tail of the data is broader than the fit and contributes more area. Thus, the R_E value obtained results in an overestimate of L_3- to L_2-intensity ratios and is therefore taken as an upper limit. The upper limit to R_E thus obtained by a Lorentzian fit is less, for iron, than is the upper limit obtained by the modified-area-ratio method, whereas for the more separated Co, Ni, and Cu L_3 and L_2 peaks the modified-area-ratio method gives a lower upper bound than does a Lorentzian fit.

A Lorentzian fit is also used for chromium. For chromium, a good fit of the data to a Lorentzian superposition is obtained. Thus, for Cr, the R_E value obtained by a Lorentzian fit is taken as a "best" value rather than an upper limit.

For Ti, the modified-area-ratio method cannot be applied consistently because there is no well-defined minimum between peaks. A Lorentzian fit to the data is poor because of the peculiar features of the Ti band structure. For Ti, a peak-height-ratio method is used to give an upper bound on the R_E ratio as described next.

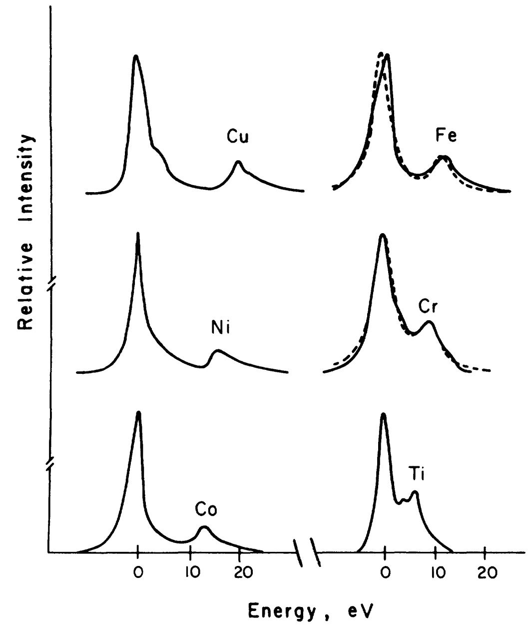

FIG. 2. Experimental $2p \rightarrow 3d$ SXS spectra for Cu, Ni, Co, Fe, Cr, and Ti, and Lorentzian fits for Fe and Cr.

For an upper limit on R_E for Ti, one again uses the fact that the L_2-peak width must exceed the L_3-peak width. The procedure used for placing an upper bound on the Ti R_E value is then as follows: First, the height of the experimental curve is measured at an energy Δ above the L_2-peak position, where Δ is the L_3-L_2 separation. If r is an upper limit approximation to the L_3- to L_2-peak-height ratio, one then obtains the relationship

$$r = I_{L_3}/(I_{L_2} - I_{L_2+\Delta} r) , \tag{3}$$

where $I_{L_2+\Delta}$ is the peak height measured at an energy Δ above the position of the L_2 peak. The quantity $I_{L_2+\Delta} r$ is an upper limit to the enhancement of the observed L_2 peak due to the L_3 peak. With use of measured peak heights, Eq. (3) is solved for r. To convert partially from a peak-height ratio to a more correct area ratio, r is then corrected to r' using the relationship

$$r' = r \frac{\text{width of } L_3}{(\text{width of } L_3) + (\Gamma_2 - \Gamma_3)} . \tag{4}$$

This r' value is then inserted into the intensity ratio of Eq. (2) and one solves for an upper limit to R_E.

Figure 2 shows the data for all the elements, plus Lorentzian fits for Cr and Fe. Figure 3 shows the extracted R_E values, compared to a related quantity obtained from SXAPS,[16,17] where the SXAPS data is discussed in the next section. SXAPS values for Ni vary greatly between studies and therefore Ni SXAPS data are not included.

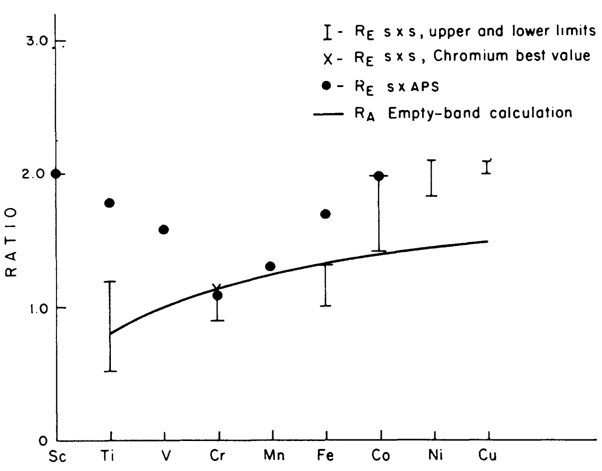

FIG. 3. R_E values compared to SXAPS L_3- L_2-intensity ratios and a calculation of R_A in the "empty-$3d$-band" approximation.

IV. COMPARISON TO APPEARANCE POTENTIAL SPECTROSCOPY RESULTS AND TO AN "EMPTY BAND" CALCULATION

It turns out that there exist data from appearance-potential spectroscopy that can be used to yield R_E values that are related to those obtained from SXS. For elements for which spectra obtained using both soft-x-ray appearance-potential spectroscopy (SXAPS) and Auger-electron appearance-potential spectroscopy (AEAPS) are measured as part of the same experiment, one can separate the effect of the x-ray-absorption event from the x-ray-emission event in SXAPS. This technique depends on the fact that, since filling an L_3 or L_2 core hole by an Auger process is of order $\sim 10^3$ more probable than by an x-ray process, for $3d$ TM APS, the AEAPS L_3- to L_2-intensity ratio depends only on the x-ray-absorption L_3- to L_2-intensity ratio in APS. This argument is given in detail by Houston and Park,[16,17] who found that for the case of chromium, the x-ray-absorption L_3- to L_2-intensity ratio in APS is the statistical ratio of 2:1.

Before making the comparison between SXAPS and SXS R_E values, it should be pointed out that Coster-Kronig transitions can also affect the SXAPS spectra as well as the SXS spectra. A simple correction for the SXAPS L_3- to L_2-intensity ratio can be derived, and is given in the Appendix. For most cases, the correction in SXAPS for effects of Coster-Kronig transitions is small; Park and Houston essentially point out that the correction vanishes for $R_E = 2$.[16,17] For a case in which R_E significantly exceeds 2, however, the correction becomes large and enhances R_E. Some of the L_3- to L_2-intensity ratios obtained in SXAPS for Ni are significantly greater than 2, and therefore, for Ni the correction is important. However, values for the SXAPS L_3- to L_2-intensity ratio for Ni vary so much among different investigations that they cannot be used for meaningful comparison. Since

Coster-Kronig corrections are small for the SXAPS L_3- to L_2-intensity ratios obtained for elements other than Ni, and since the correction derived in the Appendix assumes the initial L_3 to L_2 hole ratio in SXAPS to be two to one, an assumption tested by Houston and Parks only for chromium,[16,17] it is the uncorrected intensity ratios that are plotted in Fig. 3. If the corrected values were to be plotted, the cobalt and scandium ratios would be unchanged, and chromium and iron ratios would drop to 0.85 and 1.5, respectively. These changes are not great enough to effect any of the conclusions of the present study.

Table I contains a summary of SXAPS L_3- to L_2-intensity ratios, obtained by both peak-height- and area-ratio measurements. The area ratios are to be compared to SXS R_E values. The data are not corrected for effects of Coster-Kronig transitions. The systematic data for all the TM's are taken from Park and Houston[16] and from Grant, Hooker, and Haas.[18] Data on single-crystal Ni are taken from Park,[19] with area-ratio measurements made by the present author. Additional measurements on polycrystalline Ni are taken from Grolemund and Chopra.[20] As pointed out previously, for Ni the results of various experiments are in such disagreement that no conclusion may be drawn. For elements Co and Fe, the SXAPS L_3- to L_2-intensity ratios show the same trends but are greater than the SXS R_E values, and agreement is good for Cr. For the lightest elements, however, the SXAPS L_3- to L_2-intensity ratios approach 2 in the calcium (empty-3*d*-band) limit, whereas the R_E value for Ti in SXS clearly remains below the L_3- to L_2-intensity ratio deduced from SXAPS. R_E values obtained by both SXS and SXAPS are plotted in Fig. 3.

It may be argued that differences between the SXAPS and SXS L_3- to L_2-intensity ratios in the case of light TM's are due to the fact that SXAPS is a total-yield experiment. Not only is the x-ray emission associated with the $2p \rightarrow 3d$ transition measured, but also that for the $2p \rightarrow 3s$ transition and resonance bremsstrahlung.[21] The contribution due to the latter two processes are negligible compared to that due to $2p \rightarrow 3d$ for the heavier 3*d* TM's; clearly, however, as the 3*d* band becomes depleted, the relative strength of the x-ray emission associated with the $2p \rightarrow 3d$ transition decreases. For vanadium, Hartree-Fock calculations indicate that the contribution due to x-ray emission associated with the $2p \rightarrow 3s$ transition becomes significant, and is 24% of the $2p \rightarrow 3d$ L_3- to L_2-intensity ratio.[22] The results of Pease indicate that R_E values for x-ray emission associated with the $2p \rightarrow 3s$ transition are 2,[7] and clearly, in the empty-3*d*-band (calcium) limit, the contribution, due to the $2p \rightarrow 3d$ transition, to the L_3- to L_2-intensity ratio vanishes but that of the $2p \rightarrow 3s$ remains nonzero. There appears to be no study of the L_3- to L_2-intensity ratio for resonant bremsstrahlung, but the results of Houston and Park[16] seem to indicate that, at least in the calcium limit, this ratio is also 2.

Comparison is also made to a calculation of the x-ray-absorption L_3- to L_2-intensity ratio R_A, by Zaanen *et al.*[5] This calculation neglects all influence of electrons in the 3*d* band other than the ejected electron, and thus might be germane to the x-ray-emission L_3- to L_2-intensity ratio R_E for nearly-empty-band-limit cases near Ti. For such a calculation, of course, effects of *d*-band magnetism or band filling are not included. The authors state that one effect of the other electrons in the occupied band will be to make the experimental ratio reach the statistical value of 2.0 for a filled 3*d* band at Cu, whereas their calculation cannot produce this result. It is of interest that the R_E values obtained here have precisely this stated relationship to the calculation of Zaanen *et al.* in that agreement is good for Ti and Cr, but the R_E extracted from the data reaches 2.0 for copper, whereas the R_A calculated in the empty-band approximation does not approach the statistical value.

V. COMPARISON OF X-RAY-EMISSION AND -ABSORPTION L_3 TO L_2-INTENSITY RATIOS

L_3 to L_2-intensity ratios in x-ray absorption, denoted here by R_A, have been obtained by Leapman and Grunes for a number of metals and oxides.[2] The values so obtained greatly exceed 2 for Fe and Ni, but drop down to values much less than the statistical ratio for Cu and Ti. The R_E values obtained here are also significantly less than the statistical ratio for Ti and Cr. However, R_E differs markedly from R_A for the ferromagnetic TM's. The large difference between R_A and R_E for Fe and Ni may possibly be due to a magnetic-moment effect,[4] since, as argued in the introduction, for SXS any effect of spin on the L_3- to L_2-intensity ratio of ferromagnets would be expected to be weaker than in XANES or EELS, of those materials. It should be noted that spin may also influence R_E values obtained from SXAPS, since this, like EELS, is a threshold excitation experiment. The SXAPS, R_E values do exceed the SXS R_E values for Fe and Co.

For Ni, however, there is another possible influence on R_A and R_E. Nickel approaches the case of a "one hole per atom only in the 3*d* band" metal, and as such, the core-hole exchange effects discussed by Thole and van

TABLE I. Compilation of L_3- to L_2-intensity ratios in SXAPS.

	L_3- to L_2-intensity										
Method	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Ni (110)	Ni (111)	Reference
Area ratio	2	1.8	1.6	1.1	1.3	1.7	2	2.1			16
Area ratio								2.5	2.7	2.8	19
Area ratio								3.2			20
Height ratio	2	1.8	1.6	1.3	1.5	1.9	2.7	3.2			16
Height ratio		1.8	1.7			2.0	2.5	3.9			18

der Laan,[4] which can give a marked enhancement to the L_3- to L_2-intensity ratio for Fe in x-ray absorption, should be vanishing or small for Ni. The large R_A value observed in the EELS spectrum of Ni is not explained to date. One may therefore wonder whether, for Ni, spin-orbit splitting resulting in predominantly $d_{5/2}$ holes may possibly affect the R_A value. This is a controversial point. It is, however, evident that such an effect, if present, would result in a pronounced enhancement of R_A over R_E. The unoccupied 3*d* states of Ni from a narrow "sliver" of width ~0.1 eV.[23] Clearly, even a slight splitting of $d_{5/2}$ above $d_{3/2}$ states can have a pronounced effect on the XANES or EELS spectrum, which represents the sampling only of ~0.6 3*d* holes. The spin-orbit-coupling parameter computed by Wang and Callaway is nearly 0.9 eV.[24] However, spin-orbit splitting results in a smaller effect on the R_E value, which is reduced to a value slightly *less* than 2.0. This qualitative idea can be developed with the aid of expressions for x-ray-absorption versus -emission L_3- to L_2-intensity-ratio values, due to *d*-band spin-orbit splitting, as derived by Mattheiss and Dietz,[25] as shown below.

For the case of spin-orbit splitting in a *d*-band metal, Mattheiss and Dietz obtain the following equations, expressed in terms of R_A and R_E:

$$R_A=(6h_{d_{5/2}}+h_{d_{3/2}})/5h_{d_{3/2}}\ , \tag{5}$$

$$R_E=(6n_{d_{5/2}}+n_{d_{3/2}})/5n_{d_{3/2}}\ , \tag{6}$$

where h_j and n_j refer to effective numbers of *d*-band holes and electrons, respectively. One also has the relationships

$$n_{d_{5/2}}=6-h_{d_{5/2}}\ , \tag{7}$$

$$n_{d_{3/2}}=4-h_{d_{3/2}}\ . \tag{8}$$

Assume, for the sake of argument, that the entire enhancement of R_A in Ni is due to spin-orbit splitting. For Ni metal, one has

$$h_{d_{5/2}}+h_{d_{3/2}}\simeq 0.6 \tag{9}$$

from saturation magnetic-moment measurements.[26] If one then assumes $R_A=3.3$ (from the results of Leapman and Grunes[2]), one then has five equations in five unknowns, and one can readily solve for R_E, which equals 1.94. Thus, the spin-orbit splitting leaves the emission ratio near the statistical value of 2. The present investigation shows that R_E for Ni is indeed close to 2, in agreement with expectations based on a spin-orbit-splitting model for the R_A of Ni.

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APPENDIX: COSTER-KRONIG CORRECTIONS TO R_E OBTAINED IN SXAPS

Let Γ_{x3} and Γ_{x2} be the radiative contributions to the L_3 and L_2 lifetime energy widths. Let Y_3 and Y_2 be total fluorescence yields for the L_3 and L_2 core holes, respectively. Let Γ_A be the Auger width of both holes, and Γ_{CK} the Coster-Kronig width of the L_2 core hole. Γ_A and Γ_{CK} are much greater than Γ_{x3} and Γ_{x2} and one has

$$Y_3=\frac{\Gamma_{x3}}{\Gamma_{x3}+\Gamma_A}\approx\frac{\Gamma_{x3}}{\Gamma_A}\ . \tag{A1}$$

Similarly,

$$Y_2\approx\frac{\Gamma_{x2}}{\Gamma_A+\Gamma_{\mathrm{CK}}}+\frac{\Gamma_{\mathrm{CK}}}{\Gamma_A+\Gamma_{\mathrm{CK}}}\frac{\Gamma_{x3}}{\Gamma_A}\ , \tag{A2}$$

then the observed SXAPS L_3- to L_2-intensity ratio is given by

$$\begin{aligned}\frac{I_3}{I_2}&=\frac{N_3}{N_2}\frac{Y_3}{Y_2}\\&\approx\frac{N_3}{N_2}\frac{\Gamma_{x3}}{\Gamma_A}\left[\frac{\Gamma_{x2}}{\Gamma_A+\Gamma_{\mathrm{CK}}}+\frac{\Gamma_{\mathrm{CK}}}{\Gamma_A+\Gamma_{\mathrm{CK}}}\frac{\Gamma_{x3}}{\Gamma_A}\right]^{-1}\ ,\end{aligned} \tag{A3}$$

where N_3/N_2 is the relative probability of creating an L_3 core hole versus L_2 core hole in the x-ray-absorption process. From the above discussion of AEAPS experiments, for SXAPS (but not EELS) N_3/N_2 may be close to 2. If both I_3/I_2 and N_3/N_2 are set equal to 2 in the above expression, then $\Gamma_{x3}=\Gamma_{x2}$, independent of Γ_A or Γ_{CK}. Thus, deviations in the I_3/I_2 ratio from 2 cannot simply be due to the Coster-Kronig channel, and imply that Γ_{x3} is not equal to Γ_{x2}. This point was made earlier by Park and Houston.[16,17] Expression (A3) above may be inverted, and one can solve for Γ_{x3}/Γ_{x2}. Twice this ratio will be an SXAPS equivalent of R_E in cases where x-ray emission associated with $2p\rightarrow 3d$ transition dominates the yield. For I_3/I_2 ratios of 2.0 or less, the above correction is rather small for SXAPS. However, for a ratio I_3/I_2 of 3.2 as observed by Grolemund and Chopra for Ni,[20] the value of R_E so obtained is 5.9, which is much larger than R_A. The results of the present study show that the SXS R_E for Ni is close to 2.0.

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