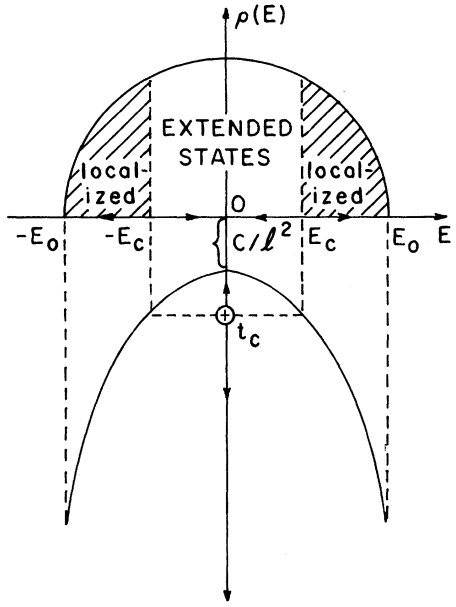

FIG. 1. Density of states $\rho(E)$ in a weakly disordered solid above two dimensions showing the existence of mobility edges at $\pm E_c$ and flow under renormalization-group transformations.

calized.

Finally, noting that t is the dimensionless resistance, we see that in Eq. (26) we have derived from first principles the β function of Abrahams *et al.*[12] ($t \propto 1/g$ of this reference). This justifies the assumption of one-parameter scaling.[13] Further we note that it is crucial for their arguments that the sign of the first correction term in the β function be negative. As we have pointed out, this follows directly from the noncompact symmetry of the model.

This work was supported in part by Brown University's Materials Research Laboratory, the National Science Foundation under Contract Nos. NSF-DMR79-20320 and NSF-DMR79-08329, the Sonderforschungsbereich 123 of The Deutsche Forschungsgemeinschaft, and The Professional Staff Congress–Board of Higher Education under Contract No. PSC-BHE-13085.

[1]F. J. Wegner, Phys. Rev. B 19, 783 (1979).
[2]R. Oppermann and F. J. Wegner, Z. Phys. B 34, 327 (1979).
[3]F. J. Wegner, Z. Phys. B 35, 207 (1979).
[4]L. Schäfer and F. J. Wegner, Z. Phys. B 38, 113 (1980).
[5]An equivalent Lagrangian has been considered by A. B. Harris and T. C. Lubensky, to be published, who discuss its properties near the upper critical dimension.
[6]E. Brézin, S. Hikami, and J. Zinn-Justin, Nucl. Phys. B165, 528 (1980).
[7]For a complete discussion of this model, see E. Brézin and J. Zinn-Justin, Phys. Rev. Lett. 36, 691 (1976), and Phys. Rev. B 14, 3110 (1976); E. Brézin, J. Zinn-Justin, and J. C. Le Guillou, Phys. Rev. D 14, 2615 (1976).
[8]A. M. Polyakov, Phys. Lett. 59B, 79 (1975).
[9]D. R. Nelson and R. A. Pelcovitz, Phys. Rev. B 16, 2191 (1977).
[10]J. Honerkamp, Nucl. Phys. B36, 130 (1972).
[11]K. Leichtweiss, Math. Z. 76, 334 (1961).
[12]E. Abrahams, P. W. Anderson, D. C. Licciardello, and T. V. Ramakishnan, Phys. Rev. Lett. 42, 673 (1979).
[13]F. J. Wegner, Z. Phys. 825, 327 (1976).

Anomalous L_3/L_2 White-Line Ratios in the 3*d* Transition Metals

R. D. Leapman and L. A. Grunes
School of Applied and Engineering Physics and the Materials Science Center, Cornell University, Ithaca, New York 14853
(Received 7 April 1980)

The L_{23} near-edge fine structure has been investigated in electron-energy-loss spectra from thin films of 3*d* transition metals and an unexpected departure from the statistical L_3/L_2 "white-line" intensity ratio of 2:1 is reported. For Ti, a ratio of 0.7:1 is observed, while for Fe and Ni the ratio exceeds 3:1, indicating a systematic trend within the period. It is suggested that many-electron effects may be important.

PACS numbers: 78.70.Dm, 73.60.Dt

In this Letter we report an anomaly in the relative excitation probabilities of L_3 and L_2 inner-core levels in the 3*d* transition metals, which we have studied with electron-energy-loss spectroscopy (EELS). At small momentum transfer the matrix element in the cross section for inelastic

scattering of fast electrons has the dipole form ($\Delta l = \pm 1$) so that the spectrum is equivalent to the x-ray absorption spectrum (XAS). Under these conditions the L_3 and L_2 edges display strongly peaked "white lines"[1] corresponding to transitions from $2p_{3/2}$ and $2p_{1/2}$ levels, respectively, to unoccupied $3d$ states of high density. Such spectral features are sensitive to electronic structure and are therefore valuable for probing chemical composition. Although the existence of these lines is well known, no systematic detailed calculations have been performed except for Ni (Ref. 2) and V (Ref. 3), primarily because of difficulties in calculating state densities several electronvolts above the Fermi level. On the basis of the $2j+1$ degeneracy of the initial core states and in a one-electron model, an L_3/L_2 white-line ratio of 2:1 is expected, as is confirmed by x-ray absorption data on the $5d$ transition elements.[4] We report striking deviations from this value and have been unable to find an acceptable explanation. Departure from a statistical ratio has been reported[5] for Pt but was attributed to spin-orbit splitting in the $5d$ band giving partly vacant $d_{5/2}$ but filled $d_{3/2}$ states. The selection rules on j forbid $2p_{1/2} \rightarrow d_{5/2}$ transitions and so the L_2 line is absent. For the $3d$ transition metals, however, the spin-orbit splitting is too small for such an effect to occur.[6]

Some x-ray absorption data exist for $2p$ excitation in the $3d$ transition elements.[7,8] However, because of experimental difficulties (thin samples and monochromator requirements), it is only recently that instrumental advances have made possible synchrotron-radiation measurements on these L edges.[9] In EELS, thin samples (a few hundred angstroms) are also necessary to avoid plural scattering by valence electrons, but uniformity need only be commensurate with the probe size ~ 2 μm or less. EELS thus offers an attractive alternative to XAS at energies $\lesssim$2 keV. No EELS measurements have been made resolving the L_{23} edges in the $3d$ transition metals, except those by Trebbia[10] for Sc, Ti, V, and Mn. We have extended these with improved resolution to Ti, Cr, Fe, Ni, and Cu.

EELS spectra were recorded in an electron-microscope–Wien-filter spectrometer system described previously.[11] A 2-μm-diam beam of 75-keV electrons is focused on the sample and allowed to pass into the energy analyzer. Such small probe sizes allow us to obtain near-edge fine structure and hence chemical information on a microscopic scale. Spectra are collected for scattering angles up to 2 mrad or 0.3 Å^{-1} momentum transfer, for which the dipole approximation is valid. The energy resolution of ~ 1.4 eV is determined by the incident-beam energy spread. Our samples were thin polycrystalline films prepared by electron beam evaporation. Thicknesses were measured as 150 Å for Ti and Cr, 100 Å for Ni, and 250 Å for Fe and Cu. These were thin enouch for plural scattering to be small near core threshold. In the case of Ti a 40-Å Cr film was evaporated on each side to protect against oxidation, which we estimate as $<10\%$ from the oxygen K-edge intensity compared with that in TiO_2 prepared by heating the metal film in air. All samples including TiO_2 were characterized by electron diffraction *in situ* before and after data collection. No significant oxide rings were detected in any of the metals.

Figure 1 shows our experimental data at the L_{23} edges with energies referenced to the L_3 threshold (Table I). The spin-orbit splitting varies from 6 eV in Ti to 20 eV in Cu. All the transition metals display strong white lines corresponding to transitions to a narrow $3d$ band and

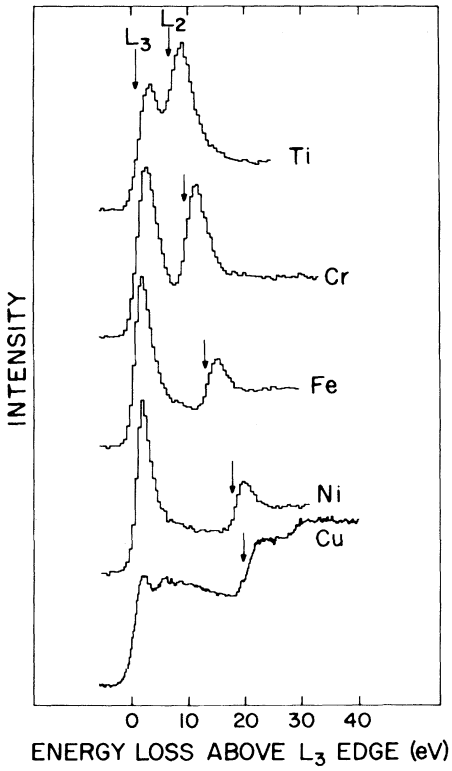

FIG. 1. L_{23}-shell excitation in the $3d$ transition metals and Cu.

TABLE I. L_{23} threshold energies, L_3/L_2 ratios, and theoretical core-level widths from Krause (Ref. 12).

Metal	Energy (eV) L_3	Energy (eV) L_2	L_3/L_2 ratio	Core width (eV) L_3	Core width (eV) L_2
Ti	458	464	0.7	0.22	0.33
Cr	575	584	1.5	0.27	0.47
Fe	706	719	3.4	0.36	0.65
Ni	855	872	3.3	0.48	0.88
Cu	931	951	2.1	0.56	1.10

we observe a decreasing L_3 linewidth across the period as this band fills, as expected. For Cu ($3d^{10}$) only steps are seen with L_3/L_2 ratio close to 2:1. We can estimate L_3/L_2 white-line intensity ratios by measuring peak areas. Each core edge can be roughly modeled as the sum of the sharp peak plus a step function due to transitions to the flat d portion of the final density of states. Our data and the calculations[2,3] show no large intensity modulations beyond the L_3 white line which could significantly alter the observed L_2 intensity. We extrapolate the step levels back from the tails of the L_3 and L_2 peaks to extract the white-line contribution. For Ti where overlap occurs, we use an iterative procedure to find the peak shapes. We obtain values of L_3/L_2 ratios of 0.8, 1.2, 3.0, and 3.1 for Ti, Cr, Fe, and Ni, respectively. Since Cu behaves statistically, this systematic anomalous trend seems specifically related to the white lines. To make a more quantitative determination of the intensity ratios, we use the following procedure. The background intensity before the edge is first subtracted empirically by fitting an inverse power law, $\propto E^{-r}$, where E is energy loss and r is a constant ~ 3. It is assumed that the observed spectrum $S(E)$ is obtained from a line shape $C(E)$, which includes instrumental broadening, evinced with strength g and h at the L_3 and L_2 energies E_3 and E_2, respectively,

$$S(E) = \int_0^\infty C(E')[g\delta(E - E_3 - E') + h\delta(E - E_2 - E')]\, dE'. \quad (1)$$

The core-edge line shape is then recovered from Eq. (1) by deconvoluting $S(E)$ by the sum of these two δ functions, giving a rigorous method of separation provided the two edges possess identical shapes. Incorrect δ-function ratios (g/h) cause residual peaks or dips at the L_2 energy as illustrated in Fig. 2 for Ni where a value of 3.3:1 is found. Values listed for the other elements in Table I agree well with the area measurements above and are accurate to within ~ ± 10%.

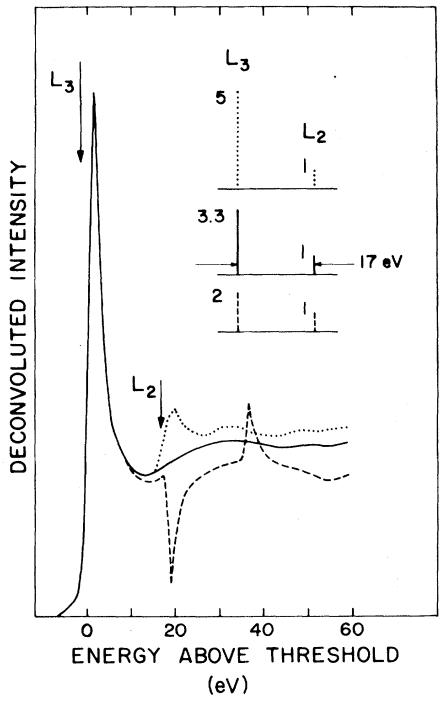

FIG. 2. Ni L_3 white-line shape obtained from deconvolution of experimental data by a pair of δ functions weighted 3.3:1 and separated by 17 eV (solid curve). Deviations from this ratio leave residual peaks (dotted curve, g/h = 5:1) or dips (dashed curve, g/h = 2:1) at the L_2 energy.

Our Ni data are consistent with XAS measurements of Bonnelle,[7] who explains an observed L_3/L_2 *peak* intensity ratio of 4:1 in terms of an increased L_2 level width. A previous one-electron calculation[2] for Ni also invokes a greater L_2 width to obtain agreement with experiment. This effect arises in the $3d$ transition metals since Coster-Kronig decay channels give a shorter L_2-hole lifetime relative to the L_3 hole. However, recent data[12] indicate that although this difference is greatest in Fe and Ni, the L_2 width exceeds the L_3 by < 0.5 eV. Taking into account our instrumental resolution we estimate the total effect on the L_3/L_2 *integrated* intensity ratio as $\lesssim$10%, which does not adequately explain our measured values. Another source of core-level broadening is multiplet splitting of the core states by their interaction with unpaired vacant $3d$ states. This effect is strongest for Cr and Fe in the middle of the period and XPS data taken far above threshold show that multiplet splitting

produces asymmetrical shoulders on the L_3 and L_2 peaks.[13] However, the XPS L_3/L_2 ratios are near 2:1 across the entire period, suggesting that final-state effects are responsible for the anomalous EELS ratios. Our spectrum for Ti agrees with EELS data of Trebbia[10] recorded at ~ 2.5 eV resolution. This author suggests the observed reversal of L_3 and L_2 intensities is only apparent and is caused by the natural linewidth being comparable with the spin-orbit splitting.

Nonstatistical results have been predicted in nonmetals,[14] and we also observe this in the $3d$-transition-metal oxides. L_{23} edges in Ti and TiO_2 are shown in Fig. 3. In the oxide both lines are split into two maxima identified[8] as due to crystal field splitting, where octahedral coordination of Ti atoms with oxygen splits the degenerate $3d$ states. A "chemical shift" of the core level by charge transfer from Ti to O modified by an excitonic shift of the final state moves the L_3 onset up in energy by ~ 2 eV in TiO_2. It is also seen that the oxide peaks in Fig. 3 are narrower and more symmetrical than the skewed line shape in the metal and this behavior is attributed to core excitons[5] in TiO_2 which is an insulator. It is interesting that the observed L_3/L_2 ratio of ~ 0.8:1 in TiO_2 as measured by the δ-function deconvolution is close to that of the metal, suggesting the importance of atomic factors. Results for the other oxides indicate that L_3/L_2 ratios are systematically higher than in the corresponding metals and these will be published separately. Kotani and Toyozawa[14] have described an excitonic theory which gives anomalously low L_3/L_2 ratios in nonmetals due to exchange interaction between two-particle states involving the hole and the photoelectron. We believe that our results also require some many-electron explanation. Recently, Citrin, Wertheim, and Schlüter[15] have shown that an anomalous L_3/L_2 jump ratio of ~ 3:1 in Na metal can be explained by spin-orbit exchange, in the same way as for nonmetals. It may be possible that an exchange interaction involving the $3d$ states occurs in the transition metals. For the $3p$ levels, which have much greater overlap with the $3d$ bands, core-hole interactions do alter the observed XAS and ultraviolet-photoelectron spectra near threshold. The $2p$ levels are, however, much more deeply bound, and hence overlap effects are expected to be smaller.[16] To assess the importance of such many-body effects, it would be useful to compare our results with one-electron calculations and recent developments now make this possible.[17]

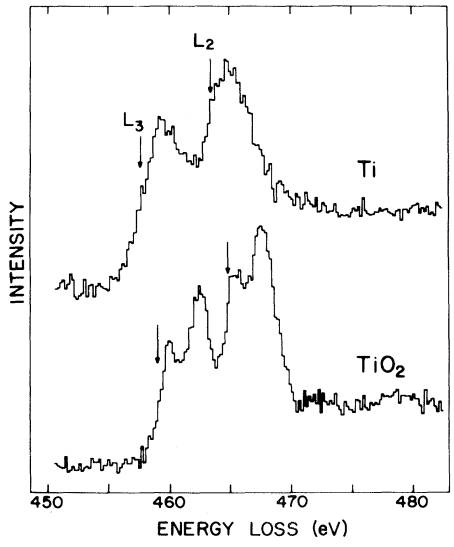

FIG. 3. Comparison of L_{23} edges in Ti and TiO_2.

In conclusion this is the first time that nonstatistical L_3/L_2 white-line ratios have been observed in a metal. This effect is much larger than the previously studied many-electron edge-singularity problem[15] and deserves further theoretical investigation. Moreover, a good understanding of variations in white-line intensities between metals and oxides could prove important for the characterization of materials on a submicron scale.

We wish to thank J. Silcox, M. S. Isaacson, V. O. Kostroun, J. E. Müller, and P. E. Batson for helpful discussions. Financial support from the National Science Foundation through the Cornell University Materials Science Center is gratefully acknowledged.

[1] L. V. Azaroff and D. M. Pease, in *X-Ray Spectroscopy*, edited by L. V. Azaroff (McGraw-Hill, New York, 1974).

[2] F. Szmulowicz and D. M. Pease, Phys. Rev. B 17, 3341 (1978).

[3] D. A. Papaconstantopoulos, D. J. Nagel, and C. Jones-Bjorklund, Int. J. Quant. Chem. Symp. 12, 497 (1978).

[4] P. S. P. Wei and F. W. Lytle, Phys. Rev. B 19, 679 (1979).

[5] M. Brown, R. E. Peierls, and E. A. Stern, Phys. Rev. B 15, 738 (1977).

[6] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, N. J., 1963).

[7] C. Bonnelle, Ann. Phys. (N.Y.) 1, 439 (1966).

[8]D. W. Fischer, J. Appl. Phys. 41, 3561 (1970).
[9]D. Denley, R. S. Williams, P. Perfetti, and D. A. Shirley, Phys. Rev. B 19, 1762 (1979).
[10]P. Trebbia, Ph.D. thesis, University of Paris-Sud, 1979 (unpublished).
[11]G. H. Curtis and J. Silcox, Rev. Sci. Instrum. 42, 630 (1971).
[12]M. O. Krause, J. Phys. Chem. Ref. Data 8, 307 (1979).
[13]S. P. Kowalczyk, L. Ley, F. R. McFeely, and D. A. Shirley, Phys. Rev. B 11, 1721 (1975); S. P. Kowalczyk, private communication.
[14]A. Kotani and Y. Toyozawa, in *Topics in Current Physics*, edited by C. Kunz (Springer-Verlag, New York, 1979), Vol. 10.
[15]P. H. Citrin, G. W. Wettheim, and M. Schlüter, Phys. Rev. B 20, 3067 (1979).
[16]R. Brühn, B. Sonntag, and H. W. Wolff, J. Phys. B 12, 203 (1979); B. Sonntag, private communication.
[17]J. E. Müller and J. W. Wilkins, to be published.

ERRATA

RADIATION-INDUCED BISTABILITY IN JOSEPHSON JUNCTIONS. Subodh R. Shenoy and G. S. Agarwal [Phys. Rev. Lett. 44, 1524 (1980)].

In Eqs. (1), (2), and (6) $T(k,\omega)$ should be $T(k,\omega_c)$. Insert a factor of $\frac{1}{2}$ on the right-hand side of Eq. (2) and above (2), substitute $K=\Omega/c'$. In the second and ninth lines below (7b), respectively, replace N by $\langle a^\dagger a\rangle$ and substitute $f_0=1+1/(2\sqrt{3Q})$, $N_{1,2}^{1/2}=N_0^{1/2}\mp\frac{1}{9}(\delta^{3/2}/Q)N_c^{1/2}$. In making numerical estimates, a bandwidth factor of $\frac{1}{15}$ has been included.

MEASUREMENT OF THE COSMIC-BACKGROUND LARGE-SCALE ANISOTROPY IN THE MILLIMETRIC REGION. R. Fabbri, I. Guidi, F. Melchiorri, and V. Natale [Phys. Rev. Lett. 44, 1563 (1980)].

The equation on page 1564, left column, line 23 should read

$$\Delta T/T=0.24\Delta I/I=(3.5^{+1.7}_{-2.2})\times10^{-5}.$$

In Fig. 3, page 1565, the abscissa label R. A. should be replaced by θ, and the axis numbers should be modified according to $0\rightarrow0°$, $4\rightarrow40°$, $8\rightarrow80°$, etc.