

Measurements of 3d state occupancy in transition metals using electron energy loss spectrometry

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We report a linear correlation between the total intensities of the $L_{2,3}$ white lines in electron energy loss spectra and the number of unoccupied 3d states in 3d transition metals. We show that this correlation can be used to obtain quantitative information about electronic changes during alloying and during solid-state phase transformations.

Data on the occupancies of 3d states can help clarify many issues fundamental to electronic theories of transition metal alloys, including phase transformations such as disorder \rightarrow order and amorphous \rightarrow crystalline.¹⁻⁴ In this letter we present a procedure for using electron energy loss spectroscopy (EELS) in the transmission electron microscope to measure the local density of 3d states for metals in the first transition series. This procedure is used to measure changes in the densities of unoccupied 3d states upon alloying for copper, nickel, and iron in $\text{Cu}_{60}\text{Zr}_{40}$, Ni_3V , and Fe_1Co_1 , respectively. We then use this procedure to measure changes in 3d occupancies during disorder \rightarrow order and amorphous \rightarrow crystalline transformations in these alloys, and we correlate these data to enthalpies of the phase transformations.

We have restricted our attention to the $L_{2,3}$ edge of the energy loss spectrum, in which an incident electron of well defined energy excites a $2p_{1/2}$ or $2p_{3/2}$ core electron to empty bound states or to continuum states. These L_2 and L_3 transitions include sharp, intense peaks known as "white lines" due to excitations to empty 3d states about the same atom. The white lines are superimposed on less intense transitions to continuum states. Because the incident, high-energy electrons are transmitted through the specimen, EELS is not surface sensitive, making it a technique for bulk density of states measurements.

Previous EELS studies have been concerned with the ratio of the L_3 to L_2 white line intensity across the 3d series. This ratio is expected to be 2:1 due to the statistical ratio of the initial states (four $2p_{3/2}$ electrons and two $2p_{1/2}$ electrons), but in practice varies with atomic number (or d band occupancy) from 1:1 to about 4:1.⁵ These anomalous ratios can be predicted in part by multiconfigurational Dirac-Fock calculations.⁶ Unfortunately for applications to charge transfer measurements, the ratio of the L_3 to L_2 white line intensity does not exhibit simple behavior with increasing d band occupancy.⁶ We chose instead to try an alternative approach of examining the sum of the L_3 and L_2 white line intensities, and correlating this sum to 3d state occupancy.

Chemically disordered foils of the binary alloys were prepared by piston-anvil rapid quenching. Thin films for the EELS analysis were prepared from these foils and from foils of the elemental transition metals by standard jet thinning and ion milling techniques. To prevent oxidation of the titanium specimen, a 40 nm film of titanium was deposited between 15 nm chromium films by direct current ion sputtering in a chamber with a base pressure of $< 1.0 \times 10^{-9}$

Torr. Electron-transparent samples were analyzed with a Gatan 607 electron energy loss spectrometer on a Philips EM 430 transmission electron microscope in diffraction mode at 200 kV using a camera length of 80 mm and a spectrometer collection aperture of 3 mm. Disorder \rightarrow order (and amorphous \rightarrow crystalline) transformations were induced in the specimens by heating them in the microscope, and EELS spectra were then recorded from the same region used for the disordered spectra. The raw data were deconvoluted to remove multiple scattering components from the spectra.⁷ All spectra were examined for oxygen edges, and when necessary samples were ion milled to remove any surface oxides (eliminating the possibility of charge transfer to oxygen 2p states). Finally, the enthalpies of the disorder \rightarrow order transformations were measured with either a Perkin-Elmer DTA-1700 differential thermal analyzer or a Perkin-Elmer DSC-4 differential scanning calorimeter.

Because the structure of the EELS spectrum near the $L_{2,3}$ edge is due to both excitations to bound states and excitations to the continuum, it is necessary to subtract the continuum contribution to determine the bound state contribution accurately. The shape of the continuum in that region is unknown, however, so we tried two empirical procedures to isolate the white line intensities. The first was to assume that the continuum onset could be modeled as a step function similar to that of the spectrum of elemental copper, which has no white lines because of its fully occupied 3d band (see Fig. 1). The first step of the function at the L_3 edge was set twice as high as the second step at the L_2 edge because we

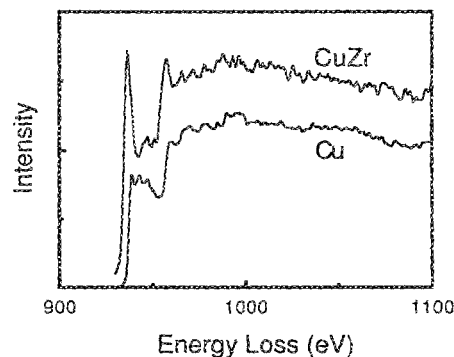


FIG. 1. EELS spectra of the copper $L_{2,3}$ edge. The upper trace is for copper in the amorphous $\text{Cu}_{60}\text{Zr}_{40}$ alloy and the lower trace is for pure copper metal.

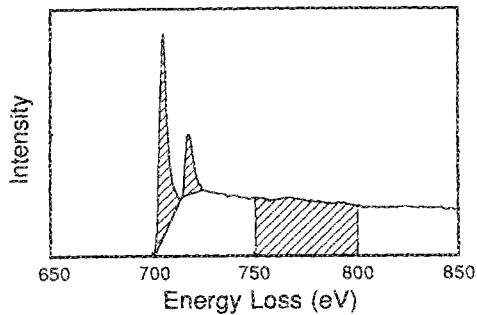


FIG. 2. EELS spectrum for pure iron showing the isolated white line intensities and the normalization energy window 50 eV in width.

expect that the 2:1 ratio of initial states should result in a 2:1 ratio for transitions from the $2p_{3/2}$ and $2p_{1/2}$ states to the continuum. The white lines were then measured by integrating the L_3 and L_2 peaks above the step function. In the second method a straight line was drawn from the base of the L_3 white line onset to the first minimum, and from there to the intersection of the falling edge of the L_2 white line and the background. The total white line intensity was then obtained by integrating the peaks above this kinked line (an example is shown for the iron spectrum in Fig. 2). In cases where the first minimum did not lie below the trailing background, the kink was only raised as high as the background immediately following the L_2 white line. For both methods the white line intensities were added together and normalized to the continuum by dividing by the number of counts in an energy window 50 eV in width which began 50 eV past the L_3 white line onset (the width of the energy window was chosen as 50 eV because it conveniently led to a maximum normalized intensity of about unity). When this normalized sum of the white line intensities, $\mathcal{L}_{2,3}$, was plotted versus position in the transition metal series, both methods provided nearly identical trends. The second method was preferred, however, for its simplicity.

The results for the $3d$ transition elements are presented in Fig. 3. The normalized sum of the white line intensities is plotted versus $3d$ occupancy in units of electrons per atom deduced by assuming that one electron occupies the $4s$ band in the metallic state. If the normalized sum of the white line intensities was linear in $3d$ state occupancy, n , and was ex-

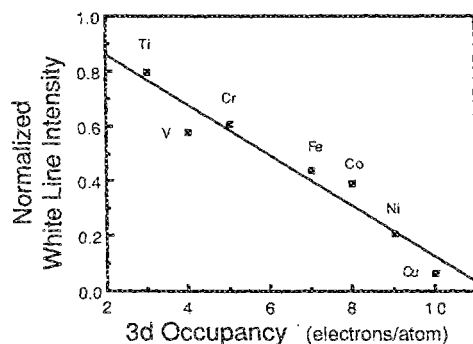


FIG. 3. Normalized sum of the $L_{2,3}$ white line intensities $\mathcal{L}_{2,3}$ vs $3d$ occupancy for seven $3d$ transition metals. The line is the least-squares fit to the data of Eq. (2).

actly zero for $n = 10$, we would expect a linear fit to the data of Fig. 1 to be

$$\mathcal{L}_{2,3} = K(1 - 0.1n), \quad (1)$$

where K is a constant. The actual least-squares fit to the data is

$$\mathcal{L}_{2,3} = 1.04(1 - 0.088n), \quad (2)$$

which is quite similar in slope, and justifies our approach of working with the sum of the white line intensities. (Although the occupancies of $3d$ states in the pure $3d$ metals do not take integer values, our use of integer values is reasonable because we seek the slope of the data in Fig. 3, and this slope should be only slightly altered by precise values of $3d$ state occupancies.) In order to determine the change in the $3d$ occupancy during alloying or during a phase transformation it is merely necessary to measure the change in $\mathcal{L}_{2,3}$ between the pure metal and the alloyed metal, or between the disordered alloy and ordered alloy, and then apply Eq. (2).

A dramatic example of a charge transfer during alloying is shown in Fig. 1 for copper in $\text{Cu}_{60}\text{Zr}_{40}$. The increased intensities of the copper L_3 and L_2 white lines in the alloy are due to a charge transfer from copper $3d$ states (presumably to zirconium $4d$ states). Application of our procedure with Eq. (2) gave a charge transfer of 0.25 ± 0.05 electrons per atom from the copper $3d$ band in going from copper metal to the amorphous alloy. This charge transfer compares favorably with that of 0.31 electrons per atom from the tight-binding calculations of Manh *et al.*⁴ We also found a charge transfer of 0.12 ± 0.05 electrons per atom back to the copper $3d$ states after the amorphous \rightarrow crystalline transformation. Similarly, we found the changes in $3d$ state occupancies for nickel in Ni_3V and iron in Fe_3Co , both upon alloying and after DO_{22} and $B2$ ordering in these alloys. These results, along with those of $\text{Cu}_{60}\text{Zr}_{40}$, are presented in Table I. The ordering enthalpies for these alloys measured by differential thermal analysis or differential scanning calorimetry, and the Miedema heats of formation for the equiatomic alloys, are also presented in Table I. The errors in the charge transfer were estimated by calculating the charge transfers for at least two independent EELS spectra from each sample, and then averaging the differences in the means. Although other electrons besides the $3d$ electrons must be considered in order to develop a complete picture of the electronic changes during alloying or during a phase transformation, it is nevertheless encouraging that the charge transfers measured in alloying and ordering correlate with the Miedema heats of

TABLE I. Changes in $3d$ occupancies after alloying and ordering, and thermochemical data.

Alloy	Change in $3d$ occupancy alloying (e/atom)	Change in $3d$ occupancy ordering ^a (e/atom)	Heat of formation (kcal/mole)	Ordering enthalpy (kcal/mole)
Cu in $\text{Cu}_{60}\text{Zr}_{40}$	-0.25 ± 0.05	$+0.12 \pm 0.05$	-9	$1.3 \pm 5\%$
Ni in Ni_3V	$+0.21 \pm 0.05$	-0.06 ± 0.05	-6	$1.0 \pm 5\%$
Fe in Fe_3Co	-0.02 ± 0.05	$+0.00 \pm 0.05$	-1	$0.9 \pm 20\%$

^a With respect to the disordered alloy.

formation and our measured ordering enthalpies, respectively, as can be seen from Table I.

We have presented a procedure by which EELS can provide quantitative information about the local occupancy of $3d$ states in transition metal alloys. Charge transfers during alloying and during solid-state phase transformations can be measured with this method. For the alloys reported here, the charge transfers during alloying and during ordering correlated well with the heats of formation and ordering enthalpies, respectively.

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¹A. R. Miedema, *Philips Tech. Rev.* **36**, 217 (1976).

²D. G. Pettifor, *Solid State Phys.* **40**, 43 (1987).

³R. E. Watson and L. H. Bennett, *Phys. Rev. B* **18**, 6439 (1978).

⁴D. Nguyen Manh, D. Mayou, F. Cyrot-Lackmann, and A. Pasturel, *J. Phys. F* **17**, 1309 (1987).

⁵R. D. Leapman and L. A. Grunes, *Phys. Rev. Lett.* **45**, 497 (1980).

⁶W. G. Waddington, P. Rez, I. P. Grant, and C. J. Humphreys, *Phys. Rev. B* **34**, 1467 (1986).

⁷J. C. H. Spence, *Ultramicroscopy* **4**, 9 (1979).