

## Observation of the two-hole satellite in Cr and Fe metal by resonant photoemission at the $2p$ absorption energy

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(Received 5 January 2000)

Valence-band spectra of Cr and Fe metal were measured with photon energies around their respective  $2p$  energies. An Auger signal is found to be superimposed on the valence-band photoemission signal for photon energies at and above the  $2p$  absorption energy, but also for excitation energies down to  $\sim 4$  eV below the  $2p$  absorption energy. This is the radiationless resonance Raman (resonant Raman Auger) regime and gives rise to a signal that is equivalent, in terms of the final state, to the 6 eV satellite in Ni with energies at 3.5 eV below  $E_F$  in Cr and 3.2 eV below  $E_F$  in Fe.

High-energy spectroscopies represent established methods for studying the electronic structure of atoms, molecules, and solids. With the advent of high-flux synchrotron radiation sources, resonance experiments such as resonance photoemission (RPE), resonance x-ray scattering, or resonance Auger spectroscopy have become interesting new tools.<sup>1-4</sup> RPE consists of performing a photoemission experiment on one electronic level with a photon energy equal to the absorption energy of another deeper core level of one of the constituents. Under this condition, one can have constructive interferences between the two channels of excitation, and the resulting intensity increase allows element-specific information to be enhanced. One condition for the occurrence of the RPE process in the valence level is the formation of a quasi-stationary intermediate state. This situation holds in solids, e.g., for rare earth compounds, because of the long-lived nature of the  $4f$  states.<sup>5</sup> It has also been found to be the case to a certain degree in Ni metal.<sup>6</sup> However, the situation is not as clear for other transition metals, although a valence-band resonance enhancement has been observed at the  $3p$  absorption energy, extending quite far above the  $3p$  energy.<sup>7-12</sup>

In the previously much-studied case of Ni metal, the valence-band resonance has been most thoroughly investigated at the energy of the  $2p$  absorption.<sup>6</sup> In short, a resonance enhancement of the valence band and the two-hole satellite about 6 eV below it have been observed for photon energies  $h\nu$  smaller than the  $2p$  absorption maximum (radia-

tionless resonance Raman spectroscopy, RRAS). For larger photon energies a normal Auger transition is observed, which is identified from its constant kinetic energy, in addition to the two-hole correlation satellite.

For  $3d$  metals to the left of Ni, less experimental data exist for resonance photoemission at both the  $3p$  and the  $2p$  resonances.<sup>7-12</sup> From measurements at the  $3p$  resonances it has been concluded that there are no two-hole satellites in the data and<sup>1</sup> (with the possible exception of Mn metal) no Auger transitions with constant kinetic energy occur for excitations with photon energies smaller than the maximum in the  $3p$  absorption coefficient.<sup>8,9</sup> While it seems to be expected<sup>1</sup> that the valence two-hole satellite does not exist in  $3d$  elements to the left of Ni metal, the detailed investigations on Ni metal around the  $2p$  edge<sup>6</sup> suggest a possible way to detect it nevertheless, namely, by using the RRAS technique. This method has also been successfully applied to investigate core-core Auger transitions in related systems.<sup>13-16</sup>

In this paper we report the first successful attempt to observe the two-hole valence-band satellite in Cr and Fe metal. In addition, an unexpected crossover from the RRAS regime to the Auger regime in these two systems is reported.

The experiments were performed at beamlines 7.0.1 and 9.3.2 of the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. The resolution in the photon channel varied between 100 meV and 230 meV, and in the

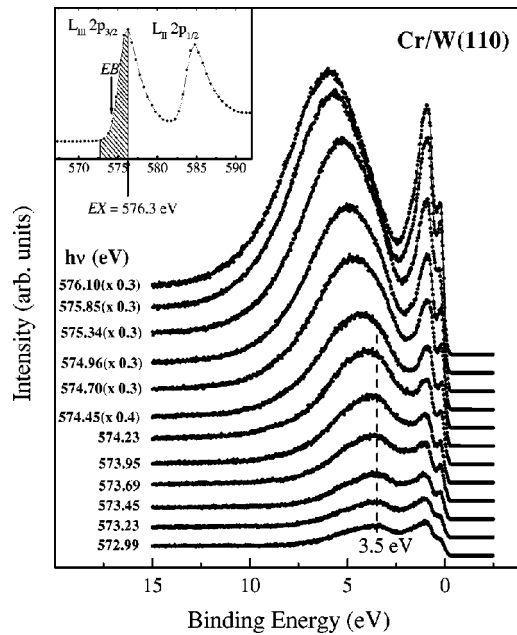


FIG. 1. Valence band photoemission spectra of Cr metal for energies leading up to the  $2p_{3/2}$  resonance absorption maximum. A large Auger signal is seen, beginning at a binding energy of about 3.5 eV and ending at the resonance maximum (photon energy equals the  $2p_{3/2}$  absorption maximum energy) of this photoabsorption spectrum at about 6 eV. The inset shows the independently measured  $2p$  photoabsorption cross section, where the photon energy range for which the electron distributions have been displayed is indicated.  $EB$  indicates the  $2p_{3/2}$  binding energy (Ref. 18). The spectra for  $h\nu=572.99$  eV to  $h\nu=574.23$  eV are given as measured, and the reduction factors for the other energies are indicated.

electron channel between 100 meV and 250 meV. The width of the  $2p_{3/2} \rightarrow 3d$  absorption line was  $\sim 2.5$  eV (measured as full width at half maximum, FWHM), and therefore, as required for straightforward analysis of the data in term of RRAS,<sup>4</sup> the width of the incoming photons was small compared to that of the resonance. The samples were thin films (80 Å to 200 Å) of pure Cr or Fe evaporated onto W(110) substrates. The quality of the sample was verified by their low-energy electron diffraction (LEED) spectra and a barely visible O  $1s$  signal. During the experiment, especially for Cr, some buildup of oxygen was observed. However, its signal in the valence-band region (at a binding energy of  $\sim 6$  eV) is well separated from that of the Cr  $3d$  spectra and could therefore be removed. The spectra ascribed to the metal did not change in any noticeable way during the period of the measurement indicating reaction of the surface with the oxygen. Also, a small second-order radiation signal was visible in the Cr spectra, and this was subtracted from the data. The energy scale was calibrated from the Fermi cutoff with an accuracy of 0.05 eV.

Figure 1 shows measured valence-band spectra for Cr metal using photon energies between 572 eV and 576 eV. The inset gives the measured photoabsorption curve for Cr, with the peak of the Cr  $2p_{3/2}$  absorption curve occurring at  $EX=576.3$  eV. The  $L_3VV$  Auger shapes could be derived from the spectra by subtracting a valence-band spectrum with a shape derived from that measured far from resonance. Similar valence-band spectra for Fe metal measured just be-

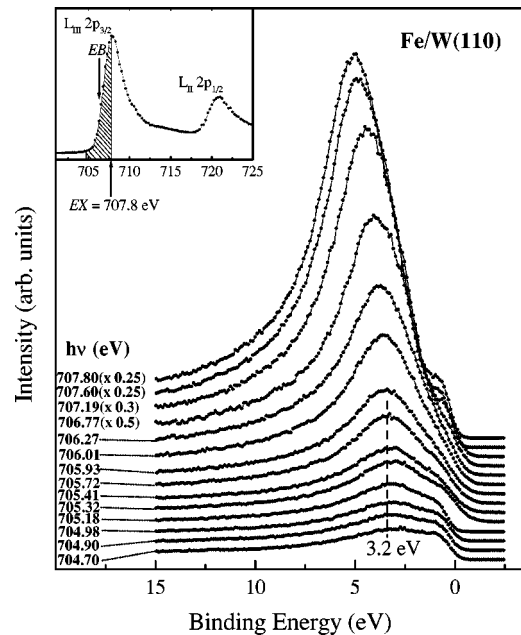


FIG. 2. As Fig. 1, but for Fe metal. Here a large Auger signal is visible, and the  $3d$  valence band intensity is barely discernible. The inset again shows the  $2p$  photoabsorption cross section, where the photon energy range for which the electron distribution has been observed is indicated, and  $EB$  indicates the  $2p_{3/2}$  binding energy (Ref. 18). The spectra for  $h\nu=704.10$  eV to  $h\nu=706.27$  eV are given as measured, and the reduction factors for the other energies are indicated.

low the  $2p_{3/2}$  energy between 704 eV and 708 eV are shown in Fig. 2, again together with the  $2p_{3/2} \rightarrow 3d$  absorption spectrum as an inset. The Fe  $2p_{3/2}$  absorption peak here is at  $EX=707.8$  eV. The valence-band spectra presented in Figs. 1 and 2 were thus recorded for photon energies leading up to the  $2p_{3/2}$  resonance energies. The  $2p_{3/2} \rightarrow 3d$  absorption energies were calibrated at a special beamline in a transmission experiment.

The valence-band spectra consist of a genuine  $3d$  valence-band feature, starting at the Fermi energy, and an Auger signal that ends up at around 5–6 eV apparent binding energy for the maximum photon energy used, which is approximately at the  $EX$  absorption maximum (top spectra in both figures). In the normal resonant Raman regime, the Auger signals should stay at constant binding energies up to  $EX$  because they track with the photoelectron peaks only; however, this is obviously not the case down to  $\sim 2$  eV below the resonance energy.<sup>4</sup>

To emphasize this point, Fig. 3 shows a few selected valence-band spectra for Cr metal, namely at the resonance energy (576.3 eV) and for two photon energies below and above the absorption maximum. For Ni metal the Auger line starts to “move” relative to the photoelectron peaks only at the absorption maximum because of its constant kinetic energy. However, for Cr the Auger spectrum starts to exhibit a constant kinetic energy and move through the binding energy spectrum already at 2 eV below the absorption resonance maximum. The spectra also show the expected intensity enhancement by factors of about 15 and 10 for Cr and Fe, respectively, at the resonance.<sup>7–11,17</sup>

In Fig. 4, a plot of the  $L_3VV$  Auger kinetic energy is presented as a function of the photon energy relative to that at the  $2p_{3/2}$  resonance maximum  $EX$ . The data for Ni are

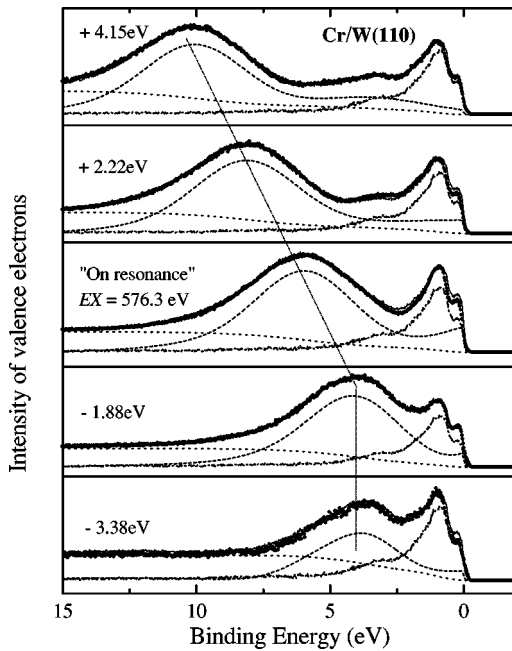


FIG. 3. Selected valence band spectra of Cr around the  $2p_{3/2}$  energy (576.3 eV) in order to show the shift of the Auger energy with photon energy (and the absence of it) below the  $2p_{3/2}$  absorption energy. The underlying dashed curves and points represent a simulation of the spectra using the Auger spectrum, the background, and the valence spectrum derived from measurements at a photon energy where they are well separated from each other.

from a previous study,<sup>6</sup> and the resonance positions for Cr and Fe metal have been determined in separate x-ray absorption measurements (insets in Figs. 1 and 2). The data for Ni metal show the linear behavior that is characteristic of the resonant Raman effect<sup>6</sup> for  $h\nu < EX$  (with  $EX$  the energy at the  $2p_{3/2}$  absorption maximum), while for  $h\nu \geq EX$  the normal Auger signal with constant kinetic energy dominates the spectra. Careful inspection of the data for Ni from 0.0 eV to about 0.6 eV below the resonance shows a small systematic deviation from the straight line, suggesting that the constant-kinetic-energy limit may be reached slightly below the resonance maximum, as noticed by the authors, who discuss several possible reasons for this behavior. However, for Ni, an important point is that the two straight lines connecting the energies below and above the resonance maximum intersect exactly at zero as defined by the photon energy relative to the resonance maximum, which is for the case equal to the  $2p_{3/2}$  binding energy.

The behavior for Cr and Fe in Fig. 4 is different, in that the “ordinary” Auger signal at nearly constant kinetic energy is observed down to about 2 eV below the absorption maximum for both cases. We stress again that the width of the exciting photons never exceeded 230 meV and is thus small compared to the  $2p_{3/2} \rightarrow 3d$  absorption curves for both Cr and Fe.

The data in Fig. 4 contain two new observations, namely, the first observation of the two-hole satellite in Cr and Fe at 3.5 eV and 3.2 eV below  $E_F$  respectively, compared to 6 eV in Ni,<sup>6</sup> and the fact that the crossover from the RRAS regime to the Auger regime is different in the three metals. With respect to the observation of the two-hole satellite we note that this feature has been sought ever since the 6 eV satellite in Ni metal was detected more than two decades ago. The

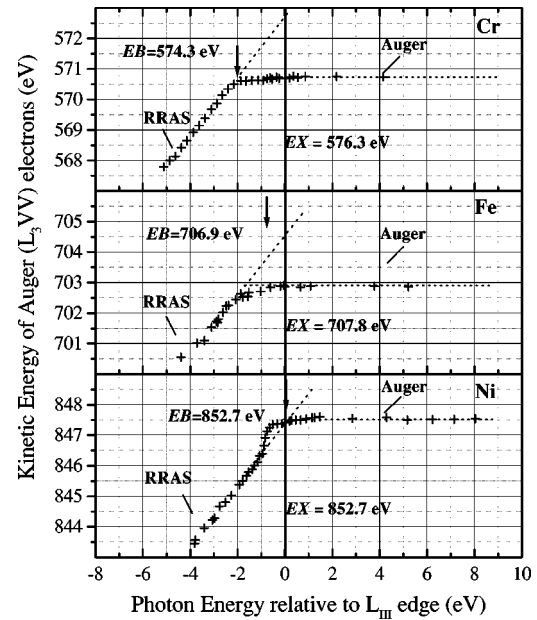


FIG. 4. Plot of the peak of the  $L_3VV$  Auger kinetic energy for Cr, Fe (this work) and Ni (Ref. 6) relative to its energy at the  $2p_{3/2}$  maximum absorption energy, as a function of the difference in photon energy from that of the  $2p_{3/2}$  absorption maximum. The dashed lines show the extrapolation of the resonant Raman Auger regime (and the Auger kinetic energy) to zero relative photon energy, and emphasize the difference between Ni on the one hand and Cr and Fe on the other hand. The  $2p_{3/2}$  binding energies (Ref. 18) are indicated by arrows, the energy of the maximum of the  $2p_{3/2} \rightarrow 3d$  absorption crosssection is given by  $EX$ ; they have been measured directly by J. Underwood at beamline 6.3.2 at the ALS, because the literature (Ref. 19) arbitrarily sets these energies equal to  $EB$ , which is obviously not correct.

crossover from the RRAS regime to the Auger regime is “normal” in Ag, Pd, Rh, and Ru, the  $4d$  equivalents to Cu, Ni, Co, and Fe, where, however, the screening dynamics is different from that in a metal<sup>13</sup> and again core-core transitions were investigated.

In principle, the crossover from the RRAS to the ordinary Auger regime could occur at the photoemission binding energy, which is the smallest energy needed to excite an electron from a core level to the valence band. This is observed in the present case in Ni and Cr as done earlier for Ag, Pd, Rh, and Ru.<sup>14–16</sup>

In addition, for Ni  $EB$  and  $EX$  agree, as in Ag, Pd, Rh, and Ru,<sup>14–16</sup> while in Cr and Fe  $EX$  is larger than  $EB$  (see Table I). This may be explained in the following way. In

TABLE I. XPS binding energies and XAS absorption energies (peak maximum) for the  $2p_{3/2}$  level of Cr, Fe, and Ni. The binding energies are the average of the numbers in Ref. 18, and the absorption energies for Cr and Fe have been determined by J. Underwood at the metrology beamline of the ALS (beamline 6.3.2), and that for Ni has been taken from Ref. 6; errors are  $\pm 0.2$  eV;  $\Delta$  is the difference between the absorption and the binding energy.

	Binding energy (XPS)	Absorption energy (XAS)	$\Delta$ (XAS-XPS)
Cr $2p_{3/2}$	574.3 eV	576.3 eV	2.0 eV
Fe $2p_{3/2}$	706.9 eV	707.8 eV	0.9 eV
Ni $2p_{3/2}$	852.7 eV	852.7 eV	0.0 eV

Ni, which is  $\sim d^9$  in the initial state, the x-ray absorption spectroscopy (XAS) experiment “removes” the one final hole from the valence band, and since one hole cannot correlate with itself, the Ni XAS process can be viewed a one-particle process.<sup>20</sup> Since in this view ( $Z+1$  approximation) the final states in photoelectron spectroscopy (PES) and XAS are the same (namely  $d^{10}$ ), the spectra of these two techniques should be similar, which they are. In Cr ( $d^4$  initial state) and Fe ( $d^6$  initial state), the XAS process can be viewed as removing one hole from a correlated six-hole and four-hole state, respectively, which means that the correlation energy has to be supplied by the incoming photon, in addition to the binding energy, meaning that  $EX$  will be larger than  $EB$ , as observed.

The question why the crossover is observed at  $EB$  in Ni and Cr but not in Fe may have its origin in dynamical effects. In order to understand why the crossover from the RRAS regime to the ordinary Auger regime in Fe does not occur at  $EB$ , one can use the following argument. The Auger kinetic energy is given by

$$E_{kin}(CVV) = BE(C) - [BE(V_1) \times BE(V_2)] - U,$$

meaning that it is given by the binding energy of the relevant core level ( $C$ ) diminished by the energy of the self-convolution of the valence band and the two-hole correlation energy  $U$ . This equation is valid for  $h\nu \geq E_B$ . For  $h\nu < E_B$  one has to replace it by

$$h\nu = E_{kin}(CVV) + [BE(V_1) \times BE(V_2)] + U.$$

If  $E_{kin}(CVV)$  stays constant for decreasing  $h\nu$  as in Fe for photon energies below  $E_B$ , either one of the two last terms or both of them have to decrease with decreasing  $h\nu$ . The most likely candidate is  $U$ , the on-site two-hole repulsion energy, because with  $h\nu < E_B$  one may enter the adiabatic regime, leading to a delocalization of the holes and a corre-

sponding decrease of  $U$ . The difference in behavior of Cr and Fe may be explained by the difference in the electronic structure of these two metals.

The differences in the resonance behavior observed for Ni, Fe, and Cr have their origin in the differences of their electronic structure. A detailed explanation of the data beyond the qualitative arguments presented requires a complicated many-body calculation, which is beyond the scope of this work.

In conclusion, it has been demonstrated that the equivalent of the 6 eV valence satellite in Ni can be seen by the RRAS technique in Cr and Fe metal at 3.5 eV and 3.2 eV below  $E_F$ , respectively. However, while in Ni this state is accessible by the PES and Auger channel in Cr and Fe, it can only be reached via the Auger channel. In all three cases, the RRAS behavior switches to an ordinary Auger behavior if the photon energy reaches approximately the binding energy. The present data, taken together with those of Ni,<sup>6</sup> thus demonstrate how, with the help of a high-intensity third-generation synchrotron radiation source, resonance techniques that were previously limited in their applicability due to low count rates can be brought to use, thus revealing additional aspects of the electronic structure of solids.

S. H. thanks the Advanced Light Source, Lawrence Berkeley National Laboratory for its hospitality, H. Wang for a very useful discussion on resonant processes, E. Arenholz and A. Kay for assistance in setting up these experiments and some first exploratory data, and the Volkswagenstiftung for the support of his work. The effort of J. Underwood to determine  $2p_{3/2} \rightarrow 3d$  absorption spectra of Cr and Fe with samples provided by J. Kortright is very much appreciated. Work at LBNL and the ALS was also supported by the Office of Energy Research, Materials Sciences Division of the U.S. Dept of Energy under Contract No. DE-AC03-76SF00098.

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<sup>2</sup>See *Appl. Phys. A: Mater. Sci. Process.* **65** (1997), special issue on resonant inelastic soft x-ray scattering, edited by Z. W. Eberhardt.

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<sup>13</sup>Recently two papers on RRAS in NiO have appeared that show an anomalous transition from the RRAS regime to the Auger regime: M. Finazzi *et al.*, *Phys. Rev. B* **59**, 9933 (1999); M. Finazzi and N.B. Brooks, *ibid.* **60**, 5354 (1999).

<sup>14</sup>T.M. Grehk *et al.*, *Phys. Rev. B* **57**, 6422 (1998).

<sup>15</sup>W. Drube *et al.*, *Phys. Rev. Lett.* **74**, 42 (1995).

<sup>16</sup>W. Drube *et al.*, *Phys. Rev. B* **60**, 15 507 (1999).

<sup>17</sup>U. Fano, *Phys. Rev.* **124**, 1866 (1961).

<sup>18</sup>*Handbook of X-ray Photoelectron Spectroscopy* (Perkin-Elmer Corporation, MN, 1992).

<sup>19</sup>B. L. Henke, E. M. Gullikson, and J. C. Davis, *At. Data Nucl. Data Tables* **54**, 181 (1993).

<sup>20</sup>To prove this point one may look at the time reserved process, namely photoemission of  $\text{Cu}_2\text{O}$  (initial  $d^{10}$  state), which leads to a  $d^9$  final state, a one-hole state; therefore the photoemission valence band equals the one-electron (uncorrelated) density of states of this material. This is of course does not mean that  $\text{CuO}$  ( $d^9$  initial state) has an uncorrelated ground state.