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# Experimental and theoretical study of 3*p* photoionization and subsequent Auger decay in atomic chromium

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## HIGHLIGHTS

- Synchrotron radiation excited Cr 3*p* photoelectron spectrum.
- High resolution Auger decay following Cr 3*p* ionization.
- Widths of the photoionized states.
- Identification and energies of the Auger decay.

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## ABSTRACT

3*p* photoionization and subsequent low kinetic energy Coster–Kronig and super Coster–Kronig Auger decay have been studied in atomic chromium. The binding energies, line widths, and relative intensities for the transitions seen in the synchrotron radiation excited 3*p* photoelectron spectrum are determined. The high resolution $M_{2,3}M_{4,5}M_{4,5}$ and $M_{2,3}M_{4,5}N_1$ Auger electron spectra following the electron impact excited 3*p* ionization are presented and the kinetic energies, relative intensities, and identifications are given for the main lines. The experimental findings are compared with the theoretical predictions obtained from Hartree–Fock and multiconfiguration Dirac–Fock approaches.



## 1. Introduction

Chromium is a d-block element with electronic configuration of $[Ar]3d^5 4s^1$. Cr is most commonly used as a component of stainless steel (Guertin et al., 2005). The inclusion of Cr makes the alloy self-passivating by forming a hard, compact film of $Cr_2O_3$ on the surface of the metal (Ashby and Jones, 2006). Besides stainless steel, Cr compounds are used in magnetic storage media (Guertin et al., 2005) and they give characteristic vibrant colors to synthetic dyes as well as natural gems like ruby (Timberlake, 2011). Cr is also one of the about 20 elements that are essential to the human body (Timberlake, 2011) playing a role in maintaining blood sugar levels and participating in the synthesis of biomolecules. In higher quantities, however, Cr is toxic (Timberlake, 2011). Because of its wide use and importance, also the electronic structure of Cr has been studied in atomic and solid forms (Mäkinen et al., 2012, 2012; Schmidt et al., 1984; von dem Borne et al., 2000; Meyer et al., 1986; Costello et al., 1991).

In this work we have studied the 3*p* photoionization and the subsequent Auger decay of atomic chromium. The decay pathways from ground state to doubly ionized state via singly ionized intermediate state have been determined in detail. The present work continues the effort to provide basic information on the electronic structure of the core shells of industrially important metals (see e.g. Jänkälä et al., 2006, 2008, 2011; Partanen et al., 2010; Anin et al., 2012, 2013 and references therein). 3*p* photoelectron spectrum of Cr has been previously measured by von dem Borne et al. (2000). They determined majority of the binding energies for 3*p* photoelectron lines and compared them with the predicted values obtained from the non-relativistic Hartree–Fock theory.

The 3*p* photoelectron spectrum, presented previously only as a reference for solid state shift experiment (Mäkinen et al., 2012), has

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been measured using synchrotron radiation excitation. The main observed features of the spectrum are compared with the theoretical ones obtained from the relativistic multiconfiguration Dirac–Fock (MCDF) and non-relativistic Hartree–Fock (HF) theories.

The Auger spectrum following the 3*p* ionization of Cr at kinetic energy region from 0 to 40 eV has been previously measured and analyzed by Schmidt et al. (1984) using electron impact excitation. They were not able to distinguish individual transitions but concluded that the lines with symmetric profiles originate from the $M_{2,3}M_{4,5}N_1$ Coster–Kronig and $M_{2,3}M_{4,5}M_{4,5}$ super Coster–Kronig transitions, whereas a group of asymmetric lines observed in the 30–40 eV kinetic energy region was interpreted to originate from autoionization.

The Auger electron decay, which occurs after the 3*p* ionization, has been measured with electron impact and analyzed in detail. The experimental kinetic energies and line widths of the main lines are compared with the theoretical values obtained from the relativistic MCDF calculations. The comparison also suggests a new interpretation for one linegroup present in the spectrum. Besides reporting the Auger electron kinetic energies and intensities, the very high resolution of the Auger electron spectrum allowed us to determine the energies of the doubly ionized final states as well as energy splittings and lifetimes of the initial 3*p* ionized states with a high accuracy.

## 2. Experiment

The 3*p* photoelectron spectrum, presented in Fig. 1 together with the theoretical prediction, was measured at beamline I411 (Bässler et al., 2001), in MAX IV laboratory, Lund, Sweden. The main lines of the spectrum have been presented in the reference (Mäkinen et al., 2012) as part of the study of atom-solid 3*p* binding energy shift. Chromium was evaporated using inductively heated oven (approximately 1400 °C for $10^{-2}$ mbar vapor pressure) (Ross and Sonntag, 1995; Huttula et al., 2008). A pulsed heating synchronized with the electron detection was used in order to prevent the magnetic field to interfere with the measurement. A Scienta SES-100 electron spectrometer (Huttula et al., 2007) equipped with a position sensitive detector and custom software were used to acquire the spectrum at the so-called magic angle of 54.7° with respect to the polarization vector of the synchrotron radiation. The photon energy of 120 eV was chosen to provide reasonable intensity with minimal overlapping of various spectral features.

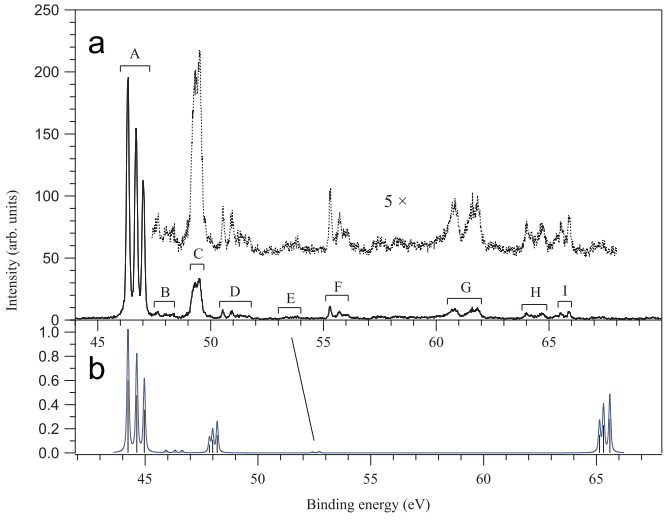


**Fig. 1.** (a) The Cr 3*p* photoelectron spectrum measured with photon energy of $h\nu$ = 120 eV. For the labels refer to Table 1. (b) The theoretically predicted Cr 3*p* photoelectron spectrum. The theoretical line intensities shown with vertical bars are convoluted with Voigt function of 60 meV Gaussian and 65 meV Lorentzian line width in order to make the visual comparison with the experiment more apparent.

Xenon and krypton gases were introduced simultaneously with the chromium vapor for the calibration of the binding energy and the transmission correction of the analyzer. Calibration of the collected data was performed using the known energies of the lines emerging from the Xe 4*d* holes (King et al., 1977) as reference points. Transmission correction was done with the aid of 3*d* photo and Auger electron lines of Kr. For more experimental details see Mäkinen et al. (2012) and Jauhiainen et al. (1994).

For the photoelectron spectrum recorded with a pass energy of 20 eV, the instrumental broadening was estimated with a Voigt type of lineshape with a width of 100 meV consisting of Gaussian and Lorentzian components of 60 meV and 65 meV, respectively. This estimation was reached by fitting lineshapes described by Voigt functions onto the Xe $4d_{5/2,3/2}$ lines. The Gaussian components were linked to each other, but the Lorentzian components were individually iterated to achieve the best fit. The known lifetimes of the Xe 4*d* lines obtained from Jurvansuu et al. (2001) were then subtracted from the Lorentzian components acquired from the fitting process.

The high resolution Auger electron spectrum following the Cr 3*p* ionization was measured with electron impact excitation at Electron Spectroscopy laboratory at the University of Oulu. The electron impact energy of 2 keV was used for ionization. The Auger spectrum was recorded with a Scienta SES-200 hemispherical electron analyzer equipped with R4000 power supply unit. The electron excitation was synchronized with the induction heating as in Huttula et al. (2009). Shortly, the electron beam was deflected off from the interaction region of the spectrometer during the heating pulses.

In order to calibrate the Auger electron energies, Xe gas was introduced simultaneously with Cr vapor. The kinetic energies of the Xe Auger transitions $N_{4,5}O_{2,3}O_{2,3}(^1S_0)$ and $N_{4,5}O_1O_{2,3}(^3P_1)$ (Carroll et al., 2002; Aksela et al., 1984) were used as reference energies. The transmission of the spectrometer was deemed to be constant within the observed energy range.

## 3. Theory

Energies and wave functions for the ground, ionized and final ionic state of the Auger transitions were obtained from relativistic multiconfiguration Dirac–Fock (MCDF) calculations using the atomic structure code GRASP92 (Parpia et al., 1996) and also from pseudo-relativistic Hartree–Fock single configuration (SC) calculations using the code of Cowan (1981).

The electron configuration of neutral Cr is $[Ar]3d^54s$. According to NIST Atomic Spectra Database (Kramida et al., 2013), the energy difference between the ground state ($^7S_3$) and the first excited state ($^5S_2$) of neutral Cr is about 940 meV. The typical temperature for evaporating Cr is between 1200 and 1400 °C. This corresponds to the thermal energy range 130–150 meV, which is significantly lower than the difference between the ground state and the first excited state in atomic Cr, thus preventing most of the thermal population of higher energy levels. This allows us to disregard the higher energy levels of the ground state configuration in the theoretical modeling.

In MCDF method, the atomic state functions (ASF) were obtained by diagonalizing the Hamiltonian matrix in the basis of jj-coupled antisymmetric configuration state functions (CSF). In case of MCDF approach, the use of Dirac–Coulomb Hamiltonian makes the method inherently relativistic, but conversion to LS-coupled basis is also possible. The radial wavefunctions were treated with the average level scheme, in which the orbitals were optimized by minimizing the average energy of the ASF by applying the GRASP92 code. Mixing coefficients of atomic states were computed with