X-Ray Absorption and Emission of Transition Elements

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Abstract :We have measured X ray spectra of 3d transition elements(Ca ,Ti ,Cr) by using high resolution crystal spectrometry. Lower Energy Satellites and radiative contributions were clearly resolved and their energies and intensities relative to parent line were determined.

Keywords: Chromium compounds, High resolution X-ray spectroscopy, Proton excitation, second order radiative contributions.

Introduction

In this paper high resolution X-ray emission and X-ray absorption spectroscopy of 3d transition metal will be discussed. To study this, emission and absorption process will be discussed. In X-ray absorption process, a core electron is excited to an empty state and the excited electron has significant kinetic energy. One can use electronic structure models such as density functional theory to determine density of states. X ray absorption gives element specific information. X ray absorption spectral shape is linear if two or more types of atom of a particular element are present. The X-ray absorption spectral shape can be described by Fermi Golden Rule. Generally the Intensity of absorption spectra is proportional to a dipole matrix element coupling the final state and the initial state. It represents the conservation of energy and Density of states is calculated with a core hole. X ray absorption spectra can be calculated by density functional theory. Multiple scattering is performed as a real space cluster calculations.

In X ray emission the electron transition of singly ionized atoms correspond to Diagram lines. These diagram lines resemble atomic one-electron level structure and are usually accompanied by the second order radioactive contributions known as Satellites. Satellites observed on lower energy side are called Lower Energy Satellite (LES). Intensity of these lines depends directly on the type of excitation. This can be explained by assuming that a Plasmon is excited during X-ray emission, emitting energy $h\omega_p$ below the parent line. Plasmon satellite exists due to sudden disturbance of electron distribution as well as due to interaction with electrons of adjacent atoms showing solid state effect or chemical effect. If Plasmon exists in Solids during X-ray emissions then High energy Satellite (HES) are observed.

X Ray Absorption:

The general fall in X-ray absorption coefficient with increasing energy of incident photon is characterized by a sharp rise when the energy is equal to the binding energy of an electron shell (K, L, M, etc.) in the absorber. This energy is the least at which a vacancy can be created in the particular shell and is referred to as the 'edge' or 'critical excitation energy'. Characteristic X-ray lines are generated when an 'initial' vacancy in an inner shell, created by X-ray or electron excitation, is filled by transfer of an electron from another shell, thus leaving a 'final' vacancy in that shell, the energy of the line is equal to the difference in binding energies of the shells with the 'initial' and 'final' vacancies. Depending on atomic number, the X-ray spectra from the elements can include lines from the K, L, M, N and O series corresponding to excitation of the K, L, M, N or O levels. The table lists the energies in kev of the principal lines of the common K, L and M series along with the corresponding

edge, or excitation, energy. Lines are identified both by the common labels like $K\alpha_1$, $K\alpha_2$, etc. and the term labels giving in order the shells with the 'initial' and 'final' vacancies e.g. KL_{III}, KL_{II}, etc. The energies of the softer radiations may be affected by the chemical state of the elements concerned generally the shifts do not exceed a few electron volts. The wavelength λ, in pm, can be derived from the tabulated energy E, in keV, by the relationship $\lambda = 1239.81/E$.

Approximate K and L line intensities are given at the head of the columns in the table, relative to the line in the series which is normally the strongest. Where a range of values is indicated, the first number represents the value for lowest Z, the second number that for the highest Z, in the section of the table to which it refers. The accompanying figure gives a plot of the relative intensities for the commonly encountered $K\beta$ line.

In addition to the lines satellite or non-diagram, lines also occur. These are generally only of significance in the case of the K-satellites or the lighter elements Al, Mg, Si, where their intensities may be a few percent of that of the $K\alpha$ line.

The transition of an electron to fill a vacancy in the K-shell may be accompanied by either the emission of an X-ray photon or the transfer of energy to another electron which is then emitted (an Auger electron); the probability that a vacancy in a given shell will result in emission of an X-ray is the fluorescence yield of that shell.

EXPERIMENT:

X-ray emission spectra either with proton or photon excitation (.i.e. PIXE or XRF) are generally used for measurements and are very effective for detecting low concentrations. The chemical state appears in the fine structure of the X-ray spectra .It is expected that $K_{\alpha 1,2}$ spectra are free from chemical effects as they are emitted through transition between inner shells. Chemical effects are more pronounced to be found in $K_{\beta 1,3}$ spectra as they are directly connected to 3d valence shell.

In this work we have focused on 3d transition element. We have measured significant chemical effects on the Intensities and energies of LES. The experiment was performed using High-Resolution crystal spectrometer. 2Mev energy was used to accelerate protons and current of 1-2 µA was applied. Lower beam current of the order of (28-75nA) was used, so that target is not damaged during proton bombardment. High-Resolution crystal spectrometer consists of a target holder, a slit, a diffraction crystal and a position detector. Emitted photons were reflected in the first order by 7.2×2.6 cm^2 Lithium Fluoride plane crystal. Reflected photons were detected by Fuji imaging plate (IP).

The diffracted X-rays formed a 2D pattern on IP detector. The horizontal axis corresponds to energy axis of spectrum. The vertical axis increases the collection area. A slit of width 1.1mm was used to get an experimental resolution close to the natural width of the observed spectral line. The distance between IP detector and the target was 858.6nm which provided excellent angular resolution. As a result $K_{\alpha 1}$ line was achieved and second order contribution of $K_{\beta 1,3}$ diagram line was easily resolved. The influence of chemical structure on $K_{\beta}L^1$ and KMM lines was investigated. The results of spectra analysis are listed in Table 1 and 2.Multiple Scattering methods are generally used for spectra of 3d transition metal systems. Multiple calculations have been carried out to show the complete spectral

shape. The metal edges don't show fine structure .It can be concluded that edges of 3d transition metal correspond to density of states. The edges energy varies from 3 to 9 Kev.

Result and Discussion:

The diffracted X-rays formed a 2D pattern on IP detector. The horizontal axis corresponds to energy axis of spectrum. The vertical axis increases the collection area. The distance between IP detector and the target provided excellent angular resolution. As a result second order contribution of $K_{\beta1,3}$ diagram line was easily resolved.

Table 1 and Table 2 represent the Intensities and energies of second order contributions in X-ray spectra. Our results confirm the energy difference between the $K_{\beta1,3}$ and K_{β}' line. The focus was on $K_{\beta5}$ line which corresponds to the dipole transition.

Table 1: Intensities of second order contributions in the $K_{\beta1,3}$ fluorescence spectra

Line	Ca	Ti	Cr
K_{β}'		28.5±1.5	38.11±0.96
$K_{\beta5}$	1.25±0.51	1.92±0.73	4.2±1.4
$K_{\beta}L^1$	4.56±0.23	3.99±0.25	5.38±0.80
KMM	1.50±0.65	1.69±0.14	1.34±0.14

Table 2: Energies (in eV) of second order contributions in the $K_{\beta1,3}$ fluorescence spectra

Line	Ca	Ti	Cr
K_{β}'		-4.92±0.23	-8.67±0.10
$K_{\beta5}$	23.1±0.6	32.5±0.91	45.4±1.5
$K_{\beta}L^1$	48.33±0.20	52.34±0.21	58.23±0.28

Conclusion:
The energy position of the $K_{\beta5}$ line relative to $K_{\beta1,3}$ line shows an increasing dependence as a function of atomic number. Our results show the decreasing dependence of KMM intensity as a function of atomic number which is verified by theoretical calculations of Scofield[13].

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