Investigating the electronic structure of pentlandite through simulation

Simon Lee, Sarah L. Harmer
School of Chemical and Physical Sciences, Flinders University, Adelaide, South Australia

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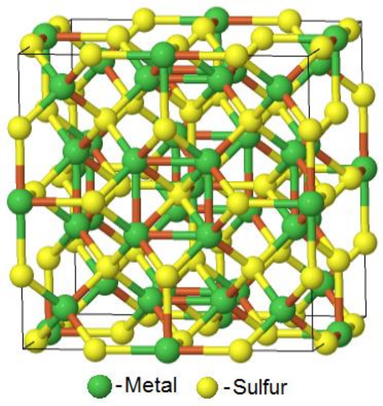
Introduction

Pentlandite $(Fe,Ni)_8S_9$ is a mineral made of iron, nickel, and sulfur. It's the world's most common source of nickel, and Australia is the world's 4th largest nickel producer[1].

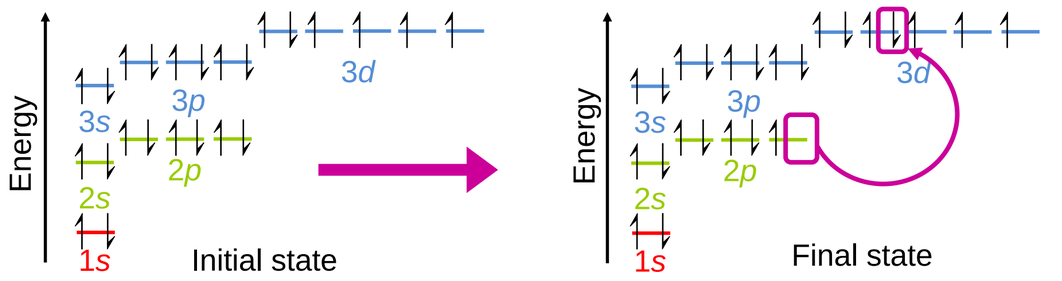


Pentlandite's crystal structure[2]

The crystal structure of pentlandite is complex but well-known. Its electronic structure however is poorly understood[3]. A better understanding of its electronic structure allows for more efficient mineral processing, and potential discoveries of novel applications.

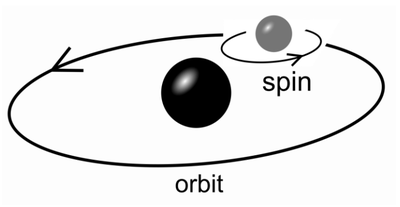
Background

The aim of this project was to simulate surface analytical data obtained of vacuum-fractured synthetic pentlandite. The charge-transfer multiplet method was used to calculate the electron energies in both iron and nickel. There are four main phenomena taken in to account in this method.

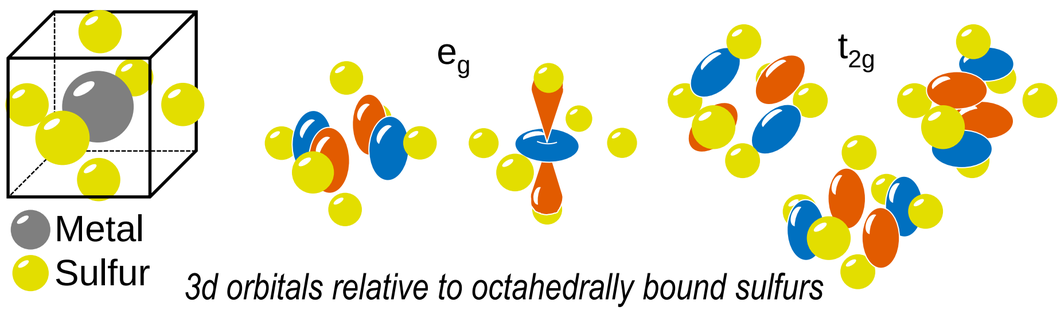


2p electron excitation process in Fe^{2+}

Firstly, when energy is imparted to an electron during an experiment it gets excited to a higher energy state. The energy difference between initial and final states is what's detected. Because of the many combinations of electron states, multiple energies can be observed, called "atomic multiplets".

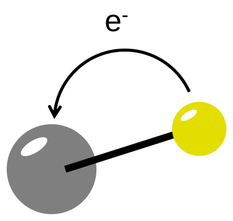


Secondly, electrons have angular momentum from both their orbit and their intrinsic spin. These combine and affect its energy.



3d orbitals relative to octahedrally bound sulfurs

Thirdly, the local crystal field is accounted for. In pentlandite, metals are either bound to 4 sulfurs tetrahedrally or 6 sulfurs octahedrally. The interaction strength between electrons in the outer metal orbitals and those in the sulfurs depends on their directionality. Stronger overlap means higher energy.



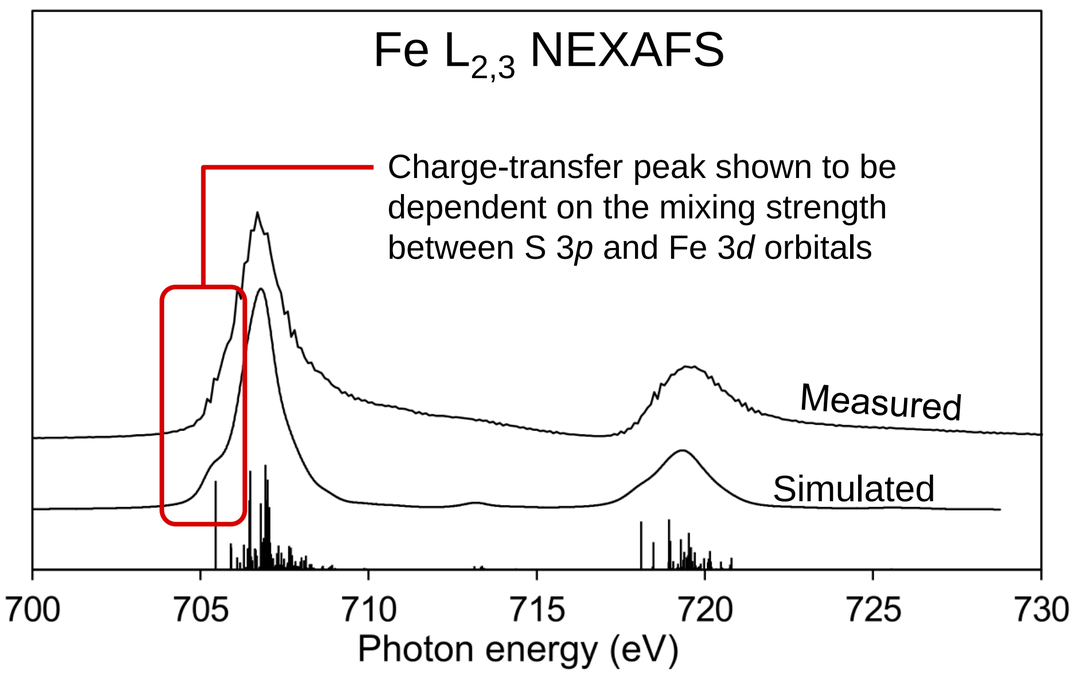
Last is the "charge-transfer" effect, where an electron moves between a sulfur and a metal it's bound to. This occurs if the system energy lowers as a result.

Results

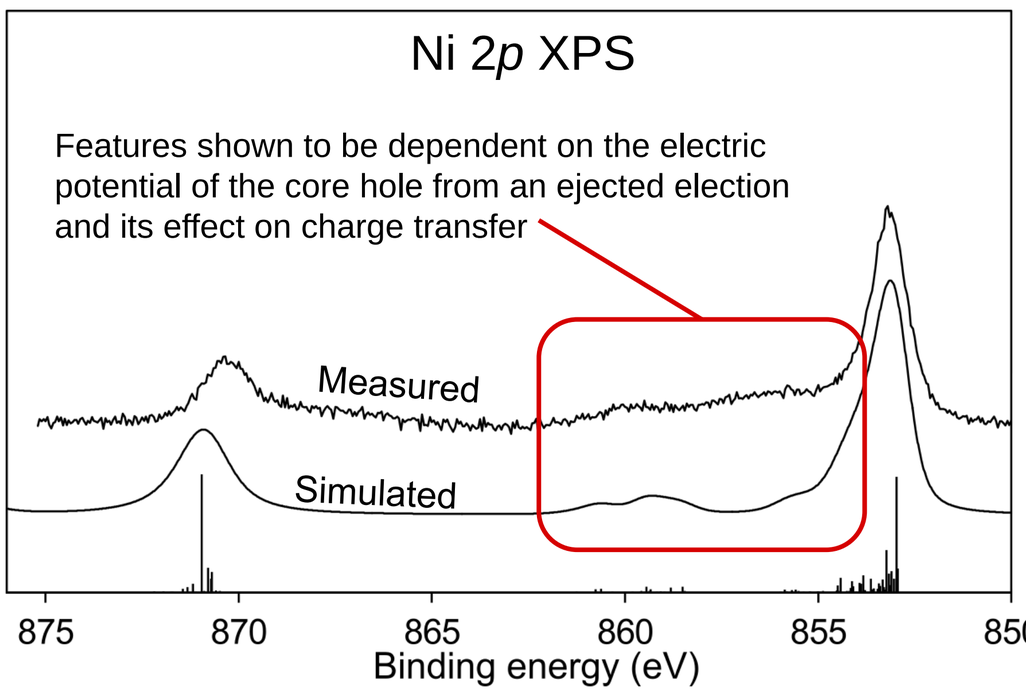
A set of electronic structure parameter values were found that successfully reproduced all the collected data.

	Multiplet splitting		Spin-orbit coupling	Crystal field splitting	Charge transfer				
F_{dd}	F_{pd}	G_{pd}	SO	$10Dq$	Δ	U_{dd}	U_{pd}	$T(e_g)$	$T(t_{2g})$
0.6	0.5	0.5	1	−0.4	1	3	4	1	2

Near Edge X-ray Absorption Fine Structure spectra were collected. This technique measures the absorption of X-rays at different energies and can give information about the unoccupied orbitals in a system.



X-ray Photoelectron Spectroscopy spectra were collected. This technique uses X-rays to measure the binding energy of electrons in occupied orbitals.



Conclusion

XPS and NEXAFS spectra of iron and nickel in pentlandite were successfully simulated using a single set of electronic parameters. Notably, the difference in energy due to charge transfer (Δ) was found to be no larger than 1eV. Features present in Fe NEXAFS and Ni XPS were shown to be due to charge transfer effects.

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References: [1] Statistia, *Major countries in worldwide nickel mine production from 2010 to 2015*, 2016
[2] Mineralatlas, *Pentlandite (Argentian Pentlandite)*, 2016
[3] Getrude Marape, *Fundamental electrochemical behaviour of pentlandite*, 2010

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