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Magnetism In 3d Transition Metals at High Pressures

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LDRD final report

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FY05 LDRD Final Report
Magnetic Transition Metals
and Oxides at High Pressures
LDRD Project Tracking Code: 02-ERD-046
Valentin Iota, Principal Investigator

Abstract

This research project examined the changes in electronic and magnetic properties of transition metals and oxides under applied pressures, focusing on complex relationship between magnetism and phase stability in these correlated electron systems.

As part of this LDRD project, we developed new measurement techniques and adapted synchrotron-based electronic and magnetic measurements for use in the diamond anvil cell. We have performed state-of-the-art X-ray spectroscopy experiments at the dedicated high-pressure beamline HP-CAT (Sector 16 Advanced Photon Source, Argonne National Laboratory), maintained in collaboration with of University of Nevada, Las Vegas and Geophysical Laboratory of The Carnegie Institution of Washington.

Using these advanced measurements, we determined the evolution of the magnetic order in the ferromagnetic 3d transition metals (Fe, Co and Ni) under pressure, and found that at high densities, 3d band broadening results in diminished long range magnetic coupling. Our experiments have allowed us to paint a unified picture of the effects of pressure on the evolution of magnetic spin in 3d electron systems.

The technical and scientific advances made during this LDRD project have been reported at a number of scientific meetings and conferences, and have been submitted for publication in technical journals.

Both the technical advances and the physical understanding of correlated systems derived from this LDRD are being applied to research on the 4f and 5f electron systems under pressure.

Introduction/Background

The electronic and magnetic interactions in transition metals are greatly affected by the spatial arrangement of the atoms in their solid phases. The strong inter-correlation between electronic structure and atomic configuration in 3-d metals is of great fundamental importance in condensed matter physics. In the case of the 3d magnetic metals (Fe, Co, Ni) and their oxides, it is believed that the polarization of the valence band holds the key to understanding the stability and the crystal structure of the element at ambient conditions [1].

By modifying the interatomic distances and potentials, applied hydrostatic pressure affects the band structure and magnetic interactions in solids. Therefore, high pressure measurements of electronic band structure combined with measurements of crystal structure can be used to quantify the contribution of the magnetic polarization to phase stability in narrow d-band metals and to understand the nature of magnetic ordering in ferromagnetic solids. In addition, understanding the contributions of the magnetic interactions to phase stability at high pressure is essential for predicting the stability and properties of planetary interior components at Earth core conditions [2, 3].

Moreover, the study of pressure-induced phase transitions in 3-d metals and oxides may offer physical insight into technologically important properties of magnetic materials. By inducing changes in inter-atomic bond lengths, applied pressure can force transition metals into metastable configurations, such as ones reported in Co and Fe nano-phases. Understanding the kinetics of phase transitions from stable to metastable structures and from magnetic to nonmagnetic phases, provides understanding of the fundamental variables controlling these changes, and offers the possibility of using those variables for engineering new materials.

Research Activities

In order to measure the magnetic moments of sample under hydrostatic pressures, we perfected a combination of X-ray spectroscopy measurements that allowed us to determine the electronic configuration, and the magnetic moments of magnetic 3d metals and oxides under pressure.

Among the advanced measurements we carried out are high-resolution X-ray Emission Spectroscopy (XES), and X-ray Magnetic Circular Dichroism (XMCD). As detailed below, we were able to solve the issue of signal absorption by the anvils in X-ray spectroscopy by using bright focused 3rd generation synchrotron sources and by measuring the K_{β} emission in a radial geometry through beryllium gaskets.

One of the difficulties in extending x-ray spectroscopic techniques to the DAC has been the strong absorption of the diamond anvils below 10keV. To avoid the attenuation

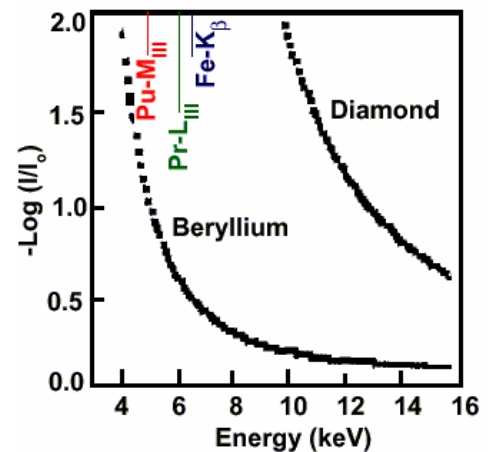


Fig 1: The use of Be gasket extends the range of XES-DAC measurements to include the 4-10keV range (covering the K emissions from 3d transition metals, the L lines in 4f rare earths as well as the M lines in 5f actinides).

of the signal in the anvils, we were able to use X-ray transparent gaskets made from high strength beryllium metal, allowing us to measure the K emission energy in radial geometry. This technique extends the range of measurable energies to cover energies down to 3keV, and will permit electronic measurements on 3d, 4f and 5f elements.

In addition, in collaboration with scientists at the APS Polarization Studies Group (beamline 4ID-D) we have developed XMCD measurements in a diamond anvil cell, by using high resolution monochromatic focused beams in conjunction with a specially designed diamond anvil cell – using partially perforated diamonds. A brief description of these two measurements is presented below.

1. X-ray Emission Spectroscopy (XES) in the diamond anvil cell:

In X-ray Emission Spectroscopy (XES) *1s* core-electrons are excited by high-energy “white” x-rays from an intense synchrotron source. The x-ray emissions are analyzed using a high-resolution (1eV) crystal analyzer to determine the spin electronic state of the sample. Because the final state of the fluorescence process is a one-hole state, XES directly probes the electronic density of states (DOS) of the valence band and is sensitive to the magnetic polarization of the 3d band as well as to chemical shifts in the core-level binding energies of the sample. For the 3-d transition elements, the K_{β} line ($3p \rightarrow 1s$ transition) contains information about the polarization of the valence band via the $3p-3d$ exchange interaction. The separation, ΔE , and intensity ratio, I'/I , of these multiplet transitions, can be used to determine the number of unpaired electrons in d-states, $2S$, and the exchange integral, J ,

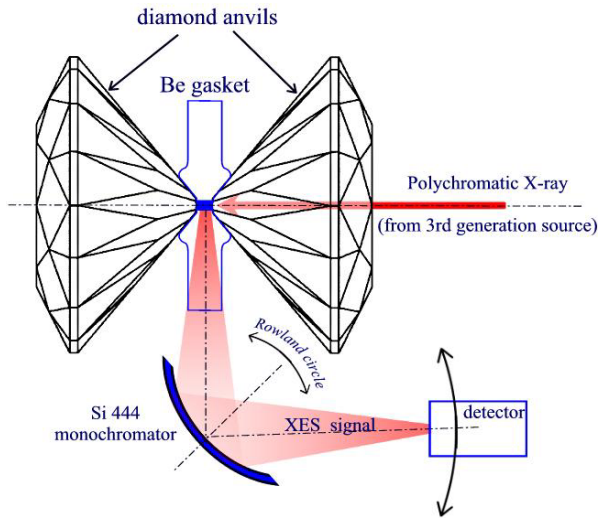


Fig 2: Experimental set-up for DAC-XES using pre-formed beryllium gaskets in axial geometry.

as $\Delta E = J(2S+1)$, and $I'/I = 2S/(2S+2)$ [4].

2. X-Ray Magnetic Circular Dichroism (XMCD) in the Diamond Anvil Cell

X-ray Magnetic Circular Dichroism (XMCD) is an element-sensitive probe of the localized magnetic moments by using polarized synchrotron radiation and quarter-wave plates to measure the spin-dependent K_{β} emission fine structures. However, while XES is sensitive to the *total* magnetization of the measured system, XMCD can discern between the contributions of different atoms in an alloy or multilayer, or between their orbital and spin moments.

The XMCD process is illustrated in the diagram in figure 3 below. For magnetic materials in the presence of an applied magnetic field, the spin up and spin down bands

are not equally populated. For an applied field in the “up” direction, there will be some empty spin up 3d states. In this case, because of conservation of spin, only the electrons with up spin can be excited into the 3d states. When the orbital motion of the 2p states is in the same sense as the circular motion of the incident light the transition probability is larger; when the two motions are in opposite directions the transition probability is smaller. *The XMCD is the difference, for a magnetic material, between the absorption of left and right circularly polarized X-rays.*

In XMCD, the atom absorbs a photon, giving rise to the transition of a core electron to an empty state above the Fermi level. The absorption cross-sections are large, especially in the energy range characteristic of 3d elements (6-8keV). The absorption edges have energies which are characteristic for each element and, due to the dipole selection rules, final states with different symmetries can be probed by choosing the initial state.

As with XES, the limiting factor in the traditional XMCD experiments in 3d elements is that the K absorption edge (~7 keV) is strongly attenuated by the diamond anvils. In addition, the small band splitting require the use of high-intensity x-rays and high-resolution detectors, unavailable until recently for use in the DAC. To avoid the absorption of XMCD signal by the diamond-anvil, the spectroscopy experiments will be conducted in a radial configuration, using hardened Be gaskets. This allows simultaneous access along the axial direction, for use for in-situ laser-heating, on-line ruby pressure measurements, or concurrent x-ray diffraction measurements. In addition, XMCD measurements require the use of external polarizing magnetic fields: to avoid interference from the DAC, the high pressure XMCD experiments will be conducted using non-magnetic (Be-Cu alloy) cells.

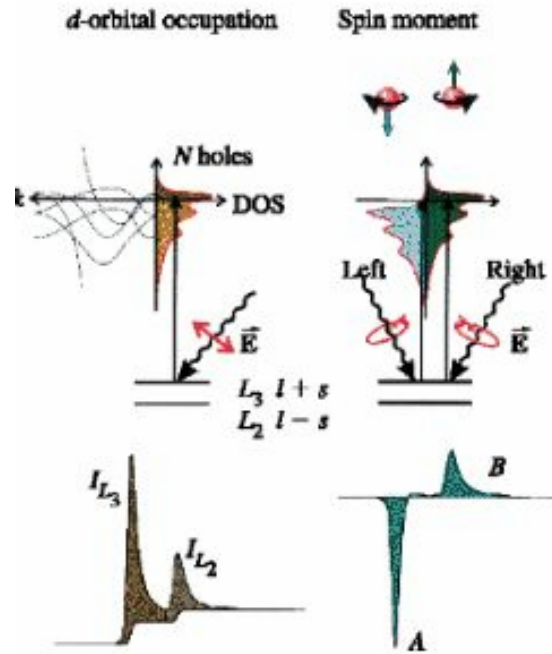


Fig 3. XMCD arises because magnetic materials have different photon absorption cross-section for left and right polarized light. The MXCD spectrum is the difference between the absorption spectra measured with the two opposite polarizations. (Diagram after J. Stöhr and R. Nakajima, IBM Journal of Research and Development, Vol. 42, 1 (1998)).

Results/Technical Outcome

1) Magnetic transitions in iron at high pressure

In iron, we have measured the K_{β} emission across the $\alpha(\text{bcc}) \rightarrow \varepsilon(\text{hcp})$ structural transition occurring at 13GPa at room temperature. In the low pressure phase (α -ferromagnetic), in addition to the main, narrow K_{β}^{1-3} peak, we observe a low energy satellite (K_{β}') – associated with transitions into the *down* spin state of the 3p orbital (i.e. in the final-state of the transition the total spin of the 3p hole is aligned opposite to the magnetic moment of the valence band).

Figure 4 shows the disappearance of the K_{β}' satellite in the high pressure phase of iron (blue spectrum in figure 4). This indicates the quenching of the magnetic moment of the Fe 3d valence electrons in the high pressure phase – suggesting that the $\alpha \rightarrow \varepsilon$ structural transition is associated with an electronic transition from a *high spin* state to a *low-spin* state. ε -Fe is non-magnetic. This result confirms the recent report by Rueff et al. [4] that the high pressure phase is *nonmagnetic* and contradicts assertions (based on direct magnetization measurements) that ε -Fe may be ferromagnetic [5].

By combining spectroscopy measurements with X-ray diffraction measurements we were able to determine in detail the electronic, magnetic and structural phase boundaries for the α - ε phase transition in iron (Fe). While our XMCD data show that the long range magnetic order (the ferromagnetism) is suppressed promptly upon the structural transition, our XES measurements reveal a diminished but measurable remnant spin in hcp-Fe up to 35 GPa. Our result is inconsistent with the proposed model of an electronically driven α - ε transition, and suggests the possibility of an antiferromagnetic or paramagnetic state of hexagonal iron at high pressures.

This result may have important consequences for current geophysical models of Earth's magnetic field, since hexagonal iron is believed to be one of the major constituents of our planet's inner core [2, 5].

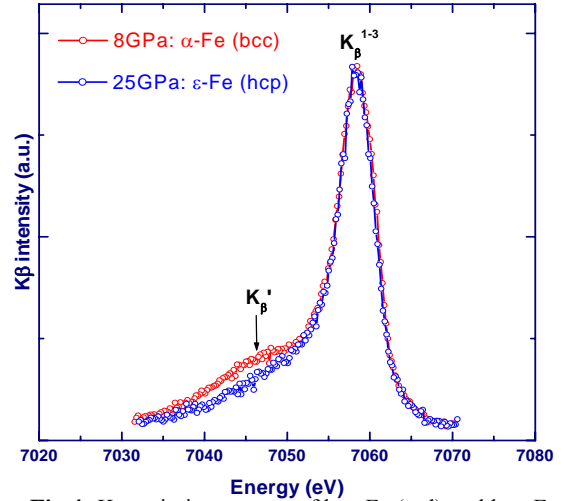


Fig 4: K_{β} emission spectra of bcc-Fe (red) and hcp-Fe (blue); the disappearance of the low energy satellite K_{β}' across the phase boundary suggests the high pressure phase is non-magnetic.

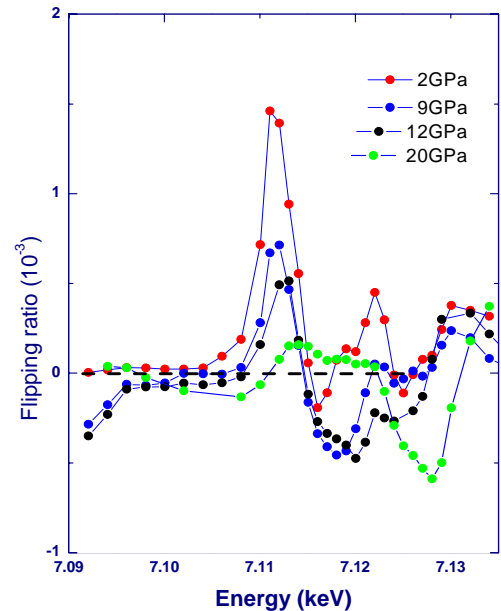


Fig 5: XMCD measurements in compressed iron show the sharp loss of long range magnetic order across the bcc-hcp structural transition.

2) Correlation-driven phase transitions dense cobalt

We investigated the spin state of cobalt up to a pressure of 125GPa by monitoring the K_{β} emission of Co (7648eV). As in the case of Fe, the low energy shoulder of the emission band results (labeled K_{β}' in figure 5) results from the exchange interaction between the $(3p\uparrow)$ final hole state and the spin polarized 3d band. For pressures below ~ 90 GPa, the K_{β} line shape remains unchanged; however, above 95GPa, and up to the maximum pressure of the experiment (125GPa) we observed a clear reduction in the intensity of the K_{β} emission. This result suggests the gradual disappearance of the 3d net spin in Co above 95GPa.

X-ray spectroscopy in high-pressure cobalt shows the quenching of both the ferromagnetism and the electronic spin at the ϵ - β phase boundary. However, in contrast with our result in iron, the structural transition is *preceded* by a significant suppression of the 3d spin. This result suggests an electronically-driven transition, where the pressure-induced increase in the 3d bandwidth is an important factor in the high pressure transformation to fcc-Co.

By simultaneously measuring angle resolved X-ray diffraction patterns of the sample, were able to correlate these changes in electronic structure with the ϵ (hcp) to β (fcc) structural phase transition in cobalt which occurs over an extended pressure range between 100-150GPa [6,7]. A comparison of the sequence of XES and XRD spectra, shows that the changes in electronic configuration *precede* the ϵ - β phase transition. This suggests that the hcp-fcc structural transformation in cobalt is triggered by pressure induced changes in the electronic configuration. A mechanism to account for the initiation of the structural transformation proposes that applied pressure induces a broadening of the 3d valence band, diminishing the electron correlations and reducing the site to site repulsions.

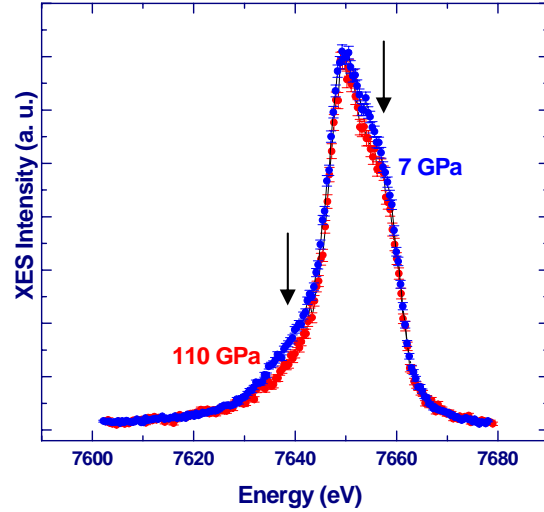


Fig 6: K_{β} emission of cobalt: spectra are collected before (red) and after (blue) laser heating to 1800K. The differences suggest electronic configuration changes accompany the ϵ - γ structural phase change.

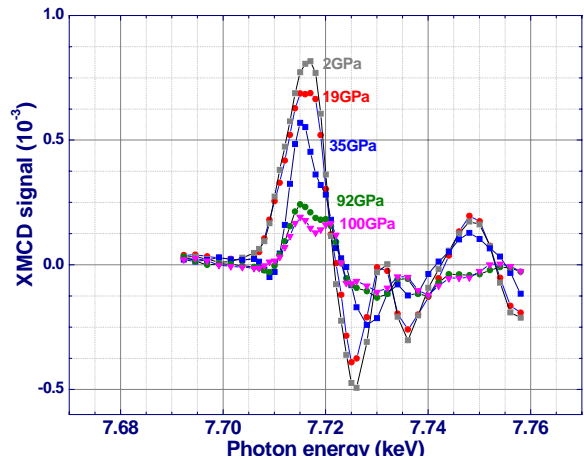


Fig 7: XMCD in compressed cobalt. The diminished dichroism with pressure suggests a reduced long range magnetic order. However, hcp-Co remains ferromagnetic up to 100GPa. The differences suggest electronic configuration changes accompany the ϵ - γ structural phase change

3) Evidence for a nonmagnetic nickel at high pressures

We performed XES measurements on nickel at pressures up to 70GPa, trying to determine the existence (and the boundaries) of a non-magnetic high density phase of Ni. The results are presented We performed $K\beta$ emission measurements on compressed nickel at pressures up to 70GPa, attempting to determine the existence (and the boundaries) of a non-magnetic high density phase of Ni. The results are presented in Fig 8.

One of the pitfalls of using XES to ascertain the magnetic (spin) state of Ni is that there is no obvious splitting in the Ni $K\beta$ band. The main reason for this is that the 3d valence band of Ni is almost full (8 spins). As a result, the net spin is much lower in Ni than either in Fe ($\sim 3\mu_B$) or in Co ($2.5\mu_B$). This is reflected in weaker exchange interaction between the 3p hole and the valence band spin, resulting in a more symmetric lineshape for the Ni $K\beta$. In conclusion, the X-ray Emission Spectroscopy of the $K\beta$ line is not sensitive enough to changes in spin state; to the limit of our sensitivity observe no changes in the line shape up to the maximum pressure (70GPa).

However, our subsequent XMCD measurements in nickel up to 70GPa show a monotonous decrease in the amplitude of the magnetic moment with pressure, suggesting the existence of a nonmagnetic nickel state above 150GPa.

Importantly, our results clearly show an increased 3d-4p hybridization with pressure in all three metals studied, suggesting that the main mechanism for magnetism suppression is band broadening of the 3d valence band [8].

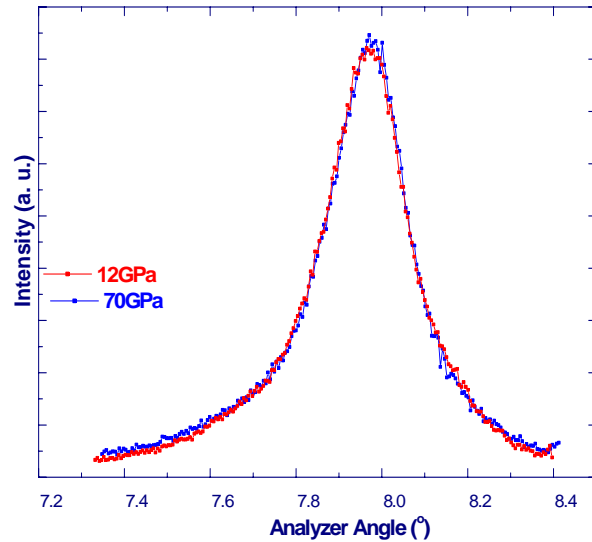


Fig 8: $K\beta$ emission of nickel up to 70 GPa. No changes are observed over the entire pressure range of the experiment. However, since Ni has a low net spin, the splitting of the $K\beta$ emission may be too weak to determine the polarization of the d-band.

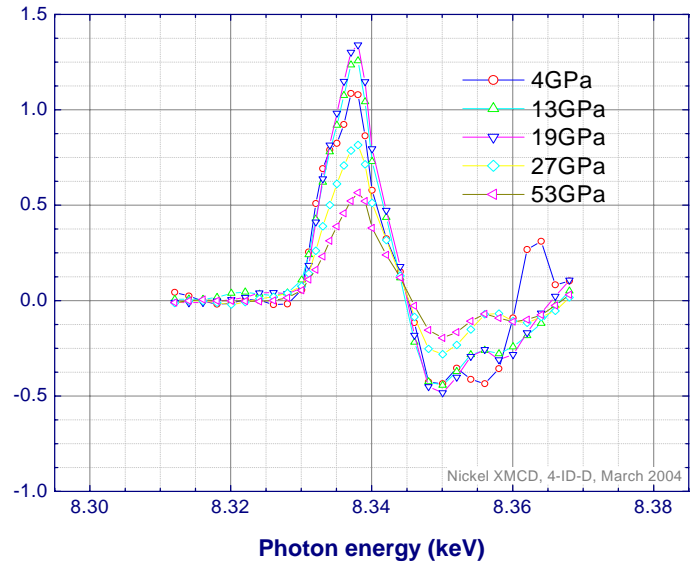


Fig 9: XMCD of nickel up to 70 GPa. We observe a diminished XMCD signal suggesting decreased ferromagnetism in compressed Ni – due presumably to pressure induced band broadening.

Exit Plan

The measurement techniques and the scientific advances made during this LDRD project can be utilized to solve other important physics problems. Currently, similar X-ray spectroscopy experiments are being used and further developed to address the complex physics issues surrounding volume collapse transitions in rare earth metals [9]. In the future, this study offers a template for studying other correlated electron systems under pressure, such as program related materials.

Summary

In this study we have investigate the electronic and magnetic properties of 3d-metals and their oxides at high pressures. The primary focus has been the study of spin transitions in iron (Fe) cobalt (Co) and nickel (Ni) and to understand he correlations between magnetism and structural properties in these 3d transition metals.

Our results show diminished magnetic spin and ferromagnetic order with pressure in all three magnetic metals studied. Based on our measurements we propose that the principal mechanism for magnetism suppression in the pressure-induced broadening of the 3d valence band.

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