

X-ray Emission Spectroscopy in Magnetic 3d-Transition Metals

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Introduction

The application of high pressure affects the band structure and magnetic interactions in solids by modifying nearest-neighbor distances and interatomic potentials. While all materials experience electronic changes with increasing pressure, spin polarized, strongly electron-correlated materials are expected to undergo the most dramatic transformations. In such materials (*d*- and *f*-electron metals and compounds), applied pressure reduces the strength of on-site correlations, leading to increased electron delocalization and, eventually, to the loss of their magnetism. In this ongoing project, we have been studying the electronic and magnetic properties of Group VIII, 3*d* (Fe, Co, and Ni) magnetic transition metals and their compounds at high pressures.

The high-pressure properties of magnetic 3*d*-transition metals and compounds have been studied extensively over the years, since iron is a major constituent of the Earth's core and because of iron's relevance to planetary modeling, as researchers try to understand planets' chemical compositions, internal structures, and geomagnetism. However, the fundamental scientific interest in the high-pressure properties of magnetic 3*d*-electron systems extends well beyond geophysical applications to include electron correlation-driven physics. The role of magnetic interactions in stabilizing the "nonstandard," ambient-pressure structures of Fe, Co, and Ni is still incompletely understood. Theoretical studies have predicted (and high-pressure experiments are beginning to show) strong correlations between electronic structure and phase stability in these materials. The phase diagrams of magnetic 3*d* systems reflect a delicate balance between spin interactions and structural configuration. At ambient conditions, the crystal structures of the α -Fe (bcc) and ϵ -Co (hcp) phases depart from the standard sequence (hcp \rightarrow bcc \rightarrow hcp \rightarrow fcc, as observed in all other nonmagnetic transition metals) with increasing *d*-band occupancy, and they are different from those of their 4*d* and 5*d* counterparts. This anomalous behavior has been interpreted in terms of the spin-polarized *d*-band altering the *d*-band occupancy [1]. At high pressures, however, the *d*-valence band is expected to broaden, resulting in the suppression or even the complete loss of magnetism. Experimentally, ferromagnetic α (bcc)-Fe has been confirmed to transform to nonmagnetic ϵ -Fe (hcp) at 10 GPa [2, 3]. Recently, we have also observed a similar transition in Co from

ferromagnetic α (hcp)-Co to likely nonmagnetic β (fcc)-Co at 105 GPa [4]. A similar structural phase transition is expected in Ni, probably in the second-order fcc-fcc transition. However, there has been no directly measured change in magnetism associated with the structural phase transition in Co, nor has such an isostructural phase transition in Ni yet been confirmed.

Similar electronic transitions have been proposed in these 3*d*-transition metal oxides (FeO, CoO, and NiO) from high-spin states (magnetic) to low-spin states (nonmagnetic) [5]. In each of these systems, the magnetic transition is accompanied by a first-order structural transition involving large volume collapse (10% in FeO, for example). So far, there have been no electronic measurements under pressure confirming these significant theoretical predictions, although the predicted pressures for the volume-collapse transitions are within the experimental pressure range (80-200 GPa).

Methods and Materials

In our experiments, we use synchrotron-based x-ray emission spectroscopy (XES) of the K β transition to determine the spin state of 3*d*-transition metals and transition metal oxides under pressure. In K β XES, 1*s* core-electrons are excited by high-energy polychromatic x-rays from a highly collimated synchrotron source: GSECARS beamline station 13-ID-D at the APS. The resulting K β emission is analyzed by using a high-resolution (1-eV) analyzer/detector system to determine the polarization of the valence band electrons. For the 3*d*-transition elements, the K β line (3*p* \rightarrow 1*s* transition) contains information about the polarization of the valence band via the 3*p*-3*d* exchange interaction. The separation ΔE and intensity ratio I'/I of the multiplet transition can be used to determine the number of unpaired electrons in *d*-states, 2*S*, and the exchange integral *J*, as $\Delta E = J(2S + 1)$, and $I'/I = 2S/(2S + 2)$ [6].

Traditionally, the limiting factor in the diamond anvil cell (DAC) XES experiments in 3*d* elements is that the K emission photons (7-8 keV) are strongly attenuated by the diamond anvils. In addition, the small band splitting requires the use of high-intensity x-rays from collimated third-generation synchrotron sources, unavailable until recently for use in the DAC. To avoid the absorption of the XES signal by the diamond anvils, our XES measurements have been conducted in a radial configuration by using hardened Be gaskets [7]. This

allows simultaneous access along the axial direction, to use for *in situ* laser heating, on-line ruby pressure measurements, or x-ray diffraction measurements.

Results

We have performed XES measurements of the $K\beta$ emission in Fe at pressures up to 50 GPa. In the low-pressure phase (ferromagnetic), in addition to the main, narrow $K\beta^{1-3}$ peak, we observed a low-energy satellite ($K\beta'$) 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 $3p$ core-hole is aligned opposite to the magnetic moment of the valence band). At pressures between 12 and 25 GPa, we observed the gradual disappearance of the $K\beta'$ satellite, indicating an electronic transition to a low-spin state. Our data show that the quenching of the magnetism in Fe occurs concurrently with the structural transformation to the high-pressure (hcp) structure (as determined from diffraction experiments). This result agrees with the report by Rueff et al. [3].

In our first experiment, we observed a small but measurable positive shift in the energy of the main $K\beta$ peak with applied pressure (~ 1 eV/GPa). However, our subsequent careful measurements, in which we used remotely controlled membrane-type DACs to avoid sample motion in the beam, did not corroborate the original results. A comparison of the two experiments suggested that the error in the original result was caused by minor but systematic changes in the beam position on the sample during the pressure increase. Our analysis also showed that the changes in beam position did not affect the intensity of the $K\beta'$ satellite band and therefore did not affect the conclusions related to the spin state of the valence band.

Figure 1 shows the results of our XES measurements under pressure on magnetite (Fe_3O_4) by using membrane DACs with Be gaskets. Our results show that between 42 and 48 GPa, the intensity of the $K\beta'$ satellite (a measure of valence band spin polarization) decreased, stabilizing at a nonzero value. We interpret this to indicate an electronic transition to an “intermediate-spin” state. Further increases in pressure did not reduce the residual intensity of the $K\beta'$ emission up to 60 GPa.

This result stands in contrast with the published XES data on hematite (Fe_2O_3) under pressure and with our own measurements of Fe_2O_3 . Our measurements indicate that in hematite, a strong suppression of the $K\beta'$ line in magnetite suggests that the final electronic state is a “low-spin” state, with paired electron spins in the valence band [8].

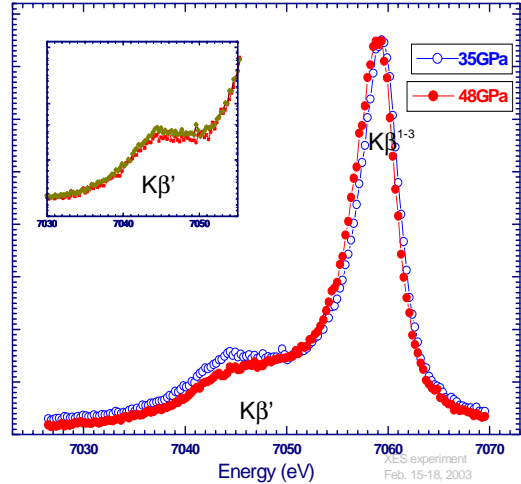


FIG. 1. XES measurements of the $K\beta$ emission in magnetite (Fe_3O_4) at high pressure. Starting around 38 GPa, the intensity of the $K\beta$ band decreases, indicating an electronic transition.

Discussion

Our analysis of the observed changes in the $K\beta$ line shape in Fe_3O_4 under pressure suggests the dissociation of magnetite into FeO and Fe_2O_3 . The resulting high-pressure phase of hematite is in a low-spin state, while the FeO maintains the polarization of the valence band at least to 143 GPa [9]. The result is an “intermediate-spin” state of the dissociated magnetite, with the observed reduced-intensity $K\beta'$ emission originating from the divalent iron sites. Above 50 GPa, the contribution of the low-spin state of Fe^{3+} to the total spin is negligible.

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