X-ray Emission Spectroscopy of 3-D Magnetic Metals under Pressure

V. Iota,[1] B. Baer,[1] C-S. Yoo,[1] H. Cynn,[1] G. Shen[2]

[1] *University of California, Lawrence Livermore National Laboratory, Livermore, CA, U.S.A.*

[2] *GSE-CARS, University of Chicago, Chicago, IL, U.S.A.*

Introduction

The study of magnetic Group III transition metals at high pressure is of fundamental importance for understanding the band structure of narrow d-band materials and the nature of magnetic ordering in these materials. In addition, the high-pressure properties of magnetic 3-*d* metals (Fe, Co, Ni) have received a good deal of attention from the geophysical community, owing to their presumed abundance in Earth's interior.[1-4]

Structural studies at high pressure have shown that the crystal structures of magnetic α-Fe(*bcc*) and ε-Co(*hcp*) phases depart from the expected sequence (hcp→bcc→hcp→fcc) observed in the non-magnetic *d*-transition metals. This anomalous behavior has been interpreted in Fe in terms of the spin-polarized *d*-band altering the *d*-band occupancy. At high pressures, the magnetism is rapidly suppressed and, as a result, ferromagnetic α(bcc)-Fe transforms to non-magnetic ε(hcp)-Fe at 10 GPa.[1] We reported recently a similar phase in Co, from the magnetic ε(hcp) to β(fcc), at 105 GPa.[2] The bulk properties (including the specific volume, bulk modulus, and crystal structure) of β-Co and their pressure dependence suggest that it is likely non-magnetic, similar to ε-Fe. However, the microscopic mechanisms of the respective phase transitions are in sharp contrast. The α→ε transition in Fe occurs reconstructively with a large volume change (~5 %), whereas the α→β transition in Co occurs martensitically over an extended pressure range between 105 and 150 GPa – without any apparent volume change. A similar, (likely second-order), phase transition has been conjectured in Ni from the *magnetic–fcc* to a *nonmagnetic–fcc* phase at high pressures,[3] but has yet to be confirmed experimentally.

Our ongoing study focuses on understanding the correlation between magnetic ordering and structural stability in 3-d metals. It is hoped that our study would help explain the high pressure phase stability of magnetic 3-d elements and help resolve the question of the proposed β- Fe (*dhcp*) phase at Earth core conditions.[4,5] The data obtained in this study will be directly compared with the first principle theoretical calculations to better understand these 3*d* magnetic elements and the Earth-core.

Methods and Materials

We have carried out x-ray emission spectroscopy (XES) together with angle resolved x-ray diffraction (XRD) measurements on Fe and Co samples, in order to establish the link between structural phase transitions and magnetic order in magnetic transition metals. A similar study will be performed on Ni samples in the future. The intensity of the K'$_\beta$ satellite in the XES spectrum is used as a marker for the presence of magnetic order in the samples;[6] the structure is identified using XRD measurements.

Results and Discussion

Figure 1 shows the disappearance of the K'$_\beta$ satellite in the XES spectrum of Fe at the α→ε transition boundary. This result

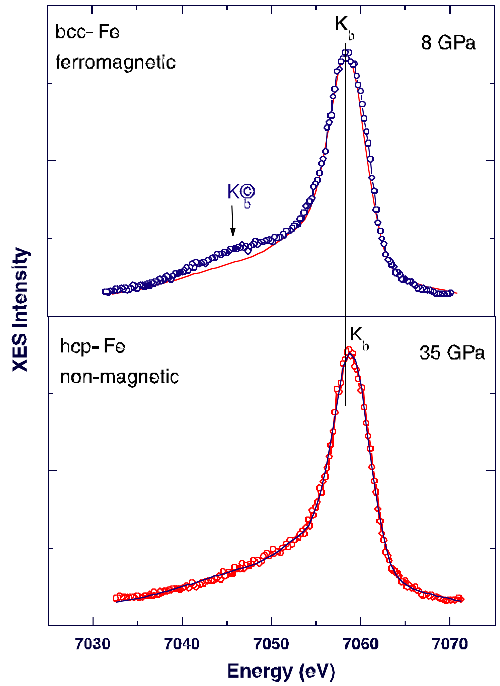

FIG. 1. XES spectrum of Fe for pressures bracketing the α→ε phase transition. The disappearance of the low-energy satellite of the K_β line at high pressure indicates the collapse of the magnetic order in ε-Fe.

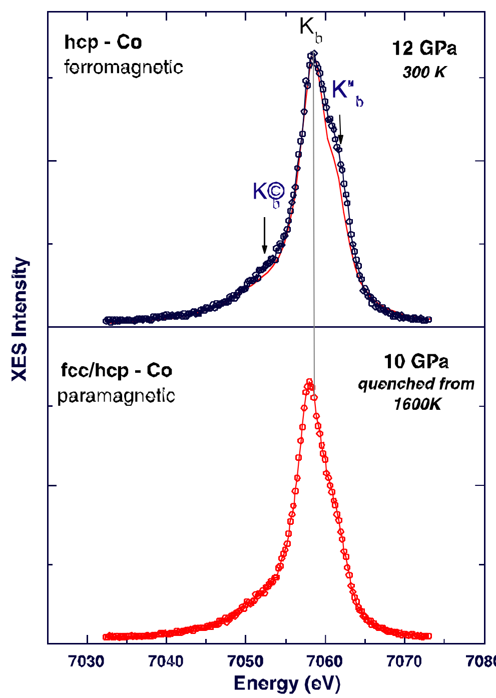

FIG. 2. XES spectrum of Co sample showing the changes in the emission spectrum before and after laser-heating the sample to 1600K. The difference between the spectra of hcp and fcc/hcp mixture are interpreted as evidence for a magnetic transition in Cobalt.

indicates the collapse of magnetic order in ε-Fe and is in agreement with previous reports.[6,7]

In our preliminary experiment, we were unable to reach the transition pressure for Co to its high-pressure (presumably non-magnetic) phase at room temperature. No changes in the XES spectrum of Co were detected for pressures up to 65GPa at room temperature. However, by laser heating the Co sample to 1600K, we were able to partially transform the sample to the high-temperature *hcp* phase. The changes in the XES spectrum associated with this transition are shown in Fig. 2. The marked drop in the intensity of the high-energy satellite on the K_β line can be clearly correlated to the structural changes in the sample. Since the conversion of the sample to the hcp structure was incomplete, we do not observe the total disappearance of the magnetic order in Co. However, this preliminary result is significant and offers *prima facie* evidence of a magnetic transition in Co (which has been conjectured but never demonstrated).[2]

Future experiments are planned to explore the correlation between magnetic order and phase stability of Co at Mbar pressures. In addition, we will investigate the existence of the second-order transition in Ni – using a similar experimental setup.

Acknowledgments

This study has been performed under the auspices of the U.S. DOE-DP by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-ENG-48 in support of the LDRD program. The XES experiments were carried out at the Advanced Photon Source, Argonne National Laboratory, supported by the DOE-OS and BES under Contract No. W-31-109-ENG-38.

References

[1] H.K. Mao et al., J. Appl. Phys. **38**, 272 (1967); J. Geophys. Res. **92**, 8129 (1987).

[2] C.S. Yoo, H. Cynn, P. Soderlind, and V. Iota, Phys. Rev. Lett. **84**, 4132 (2000).

[3] P. Soderlind et al., Phys. Rev. B **50**, 5918 (1994); Phys. Rev. B **53**, 14063 (1996).

[4] L.S. Dubrovinsky et al., Phys. Rev. Lett. **84**, 1720 (2000).

[5] C.S, Yoo et al., Science **270**, 1473 (1995); ibid Science **275**, 96 (1997).

[6] P. Rueff et al. Phys. Rev. B. **60**, 14515 (1999).

[7] R.D. Taylor, M.P. Pasternak, and R. Jeanloz, J. Appl. Phys. **69**, 6126 (1991).