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ABSTRACT

Magnetic Circular X-ray Dichroism (MCXD) studies at K edges of Fe-Ni alloys reveal changes of the MCXD signal with composition and crystal structure. We observe that the signal at the invar composition is of comparable strength as other compositions. Moreover, the edge position is strongly dependent on lattice constant. First principles calculations demonstrate that the shape and strength of the signal strongly depends on the crystal orientation, composition, and lattice constant. We find direct relation between the MCXD signal and the p DOS. We find that the MCXD at K edge probes the magnetism due to itinerant electrons.

INTRODUCTION

Iron-Nickel alloys are one of the most studied magnetic systems. The alloy undergoes a structural phase transition from bcc (Fe rich) to fcc (Ni rich) at the Fe\textsubscript{65}Ni\textsubscript{35} invar composition. Historically, the low thermal expansion was limited to fcc Fe alloys (Fe-Ni, Fe-Pt, Fe-Pd). The large spontaneous volume magnetostriction, invar anomaly, is observed in ferro-, ferri- and antiferromagnets of transition metal alloys including amorphous and weak itinerant electron ferromagnets. In the Fe-Ni alloys a low thermal expansion coefficient is observed only in the fcc region very near to the fcc-bcc phase boundary. The origin of the invar anomaly has been discussed by Weiss [1], Chikazumi [2] and more recently in reference [3].

There are significant differences in the MCXD spectra for K and L edges. The L edges measurements seems to be more accessible to theoretical modeling than the K edges and more sensitive to the local atomic properties. In this paper we investigate using MCXD the behavior of Fe and Ni in the Fe-Ni alloys by measuring the K edges. The studied alloys include the invar (Fe\textsubscript{65}Ni\textsubscript{35}) composition. The measurements are compared to full-potential linearized augmented plane wave method calculations. We show that relevant and unique information can be obtained from the K edge MCXD measurements. This is strongly related to the fact that the p wavefunctions are more extended than the d wavefunctions. The K edge measurements are very sensitive to the p DOS and consequently provide more information on the itinerant character of the magnetism. Thus they are sensitive to the crystal symmetry, lattice parameters, and neighboring atomic species.

Magnetic properties of a material arise from the combined contributions of multiple atomic species. Furthermore, for any one of these species, the various atomic orbitals make their own differing contributions to the magnetism of the solid. One of the challenges for researchers is to distinguish among these varied sources. Magnetic Circular X-ray Dichroism (MCXD) is a relatively new synchrotron technique that can provide this type of information [4,5,6]. MCXD studies the magnetism of the unoccupied states. It uniquely allows studies of very small contributions to the magnetic moment independently of other contributions present in a compound.
The MCXD consists of measuring the difference in the x-ray absorption for magnetization parallel and antiparallel to the direction of the incident circularly polarized photons as function of the photon energy across the absorption edge, $\mu_\parallel - \mu_\perp$. We use an energy dispersive beamline with a curved crystal employing a four point crystal bender [7,8]. There are several important consequences of the use of this type of a polychromator for dichroism studies. It allows us to study small samples or small areas of a sample due to a very fine horizontal focusing (about 100 µm). A polychromator spectrum contains self reference both in intensity and energy since all energies are measured at the same time. A polychromator is very stable during an energy scan since there is no movement of the x-ray optics involved. The setup satisfies the high stability required in the MCXD measurements at the K-edges where a very small signal is observed.

We show, in this paper, high quality data obtained using a unique and robust energy dispersive setup with pixel size resolution of 140 meV. Most of the previously published synchrotron-based work involved 0.5 - 1 eV step size with double crystal monochromators which are not as stable as the setup used here. Since the MCXD signal contains sharp structure, optics stability and small step size are essential for these measurements. Moreover, an unique experimental geometry is used in which magnetization is always in the direction of the incident photon. This geometry is essential because of the possible angular dependence of the MCXD features.

EXPERIMENTAL

The MCXD measurements were performed at beamline X6A at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. The experimental setup and MCXD data acquisition sequence have been previously discussed [8]. The degree of measured circular polarization (CP) after the polychromator (at the sample position) was about 97% for this slit position. The CP was measured indirectly by measuring the degree of linear polarization with a Compton polarimeter. X-ray and the magnetic field directions are collinear. The magnetic field is applied using an electromagnet which produces a field of 1.09 T at the sample position. We used commercially available polycrystalline foils of Fe-Ni alloys which were further thinned by cold rolling to an approximate thickness of 10 µm. As a reference we used Al filters.

The MCXD signal is reported as a percentage of the step height. Step height is obtained by fitting an absorption spectrum above the edge with a straight line and determining the value of the fit at the edge position. Our measurements are perpendicular to the surface of the thin foil (10 µm) and saturation fields are higher due to shape anisotropy. We achieve saturation at 0.5 Tesla in this geometry.

EXPERIMENTAL RESULTS

We measure the MCXD signals at the K absorption edges of Fe and Ni. We studied the following alloy compositions; Fe$_{52}$Ni$_{48}$, Fe$_{55}$Ni$_{45}$, Fe$_{64}$Ni$_{36}$, as well as elemental Fe and Ni [9]. With some modifications we describe the spectra following the nomenclature of reference [10]. The top parts of figure 1 show the XANES spectra at the K-edges of Fe and Ni respectively. The absorption edge energy was determined from the first inflection point of the XANES for pure metals. All K edges of Fe (Ni) were measured at the same time so the relative shifts of the edges can be precisely determined. The XANES spectrum of Fe exhibit two humps at 1 eV ($\alpha_1$) and 3 eV ($\alpha_2$) independent of the crystal structure. The third hump observed at an energy around 10 eV ($\beta_1$) in pure Fe (bcc) and at 8 eV ($\beta_2$) in the fcc crystal structure. The XANES of bcc Fe has a peak at 18 eV ($\gamma_1$) and two peaks at 16 eV ($\delta_1$) and 23 eV ($\varepsilon_1$) in fcc Fe. The latter structure is due to multiple scattering effects from higher shells.
in the bcc and fcc structures. The XANES of pure Ni has a single hump around 3 eV ($\alpha$) which becomes a double hump ($\alpha$, $\beta$) when Fe is added, a hump at 6 eV ($\beta$), and two peaks at 16 eV ($\delta$) and 23 eV ($\epsilon$). The main absorption peaks $\gamma$ of Fe (bcc) and $\delta$ and $\epsilon$ of Ni (fcc) might also be due to $1s \rightarrow 4p$ transitions [10], while the low energy humps can be assigned to a $p$-projected DOS which are strongly hybridized with 3d-states of the surrounding atoms. The overall features of the XANES spectrum at the Fe and Ni K-edges are similar in shape and strongly dependent on the crystal structure. The peaks $\beta$, $\gamma$, $\delta$, and $\epsilon$ in the XANES are sensitive to the crystal structure of the alloy while $\alpha$ is not. Moreover, we observe a systematic energy shift of the Fe K-edge to slightly higher values ($< 50$ meV) for all crystal structures. There is also a -0.42 eV energy shift of the Ni K-edge between pure Ni and the alloys. The observed shift seems to be related to the change in lattice parameter from 3.5169 Å for elemental Ni to 3.5804 Å for Ni$_{85}$Fe$_{15}$ alloy [11].

The MCXD measurements at the Fe K-edge are shown at the bottom left of Figure 1. The Ni K-edge MCXD measurements are shown at the bottom right of Figure 1. The magnetic signal is weak and constitutes only 0.1% of the absorption edge intensity. The valence band magnetic signal spans a range of about 10 to 15 eV. The MCXD spectrum of pure Fe has the following characteristic structure: a positive peak at the absorption edge, a negative peak around 5 eV, a negative peak near 11 eV, a positive peak around 18 eV, and a positive peak around 29 eV. The MCXD spectrum of pure Ni has a negative peak at the absorption edge, a negative peak at 5 eV, a negative peak at 10 eV, a positive peak around 16 eV, and a possible peak around 23 eV. The unchanging feature in the alloys is the presence of a positive and negative peak at the absorption edge. The presence of Fe is manifested by a positive peak right at the absorption edge; it is observed at the K-edges of Fe and Ni. The feature persists in all crystal structures with varied intensity. The signal systematically decreases with decreasing Fe fraction. Contrary to previous studies [10] we observe that the signal at the invar composition has comparable strength to other compositions. We attribute this to the fact that higher fields (> 1 T) are used in our measurements compared to 0.3 T used in previous studies. Moreover, we used cold rolled (disordered) foils as samples instead of powders which could randomize the composition.

Three features are to be noted in the MCXD spectra of Fe-Ni alloys. The first feature is the similarity in shape between the MCXD spectra at the Fe and Ni K-edges in the alloys. This similarity suggests that the orbital polarization at the Fe site is similar to that at the Ni site. This means that the final $4p$-states are not localized within a specific type of atom but are extended. The second feature is exhibited in the Fe concentration dependence of the MCXD spectra. We observe that strength of

![Fig. 1: XANES (top) and MCXD (bottom) spectra at Fe (left) and Ni (right) K-edge.](image-url)
the MCXD peaks is very sensitive to small changes in Fe concentration. We also observed clear evidence of the presence of a magnetic EXAFS signal. Comparison with first principles calculations shows that the shape and strength of the signal depends on the crystal orientation, composition, and lattice parameter.

THEORETICAL MODEL

We compare the experimental results to the following theoretical model. We solved the single particle Kohn-Sham equations [12] with Hedin-Lundqvist exchange-correlation energy [13] self-consistently using the full-potential linearized augmented plane wave (FLAPW) method [14]. In the FLAPW method, the core electrons are treated relativistically and the valence electrons are treated scalar-relativistically, i.e., the spin-orbit coupling (SOC) is neglected. The SOC effect for the valence states is treated in a second-variational manner in which the spin-orbit coupling Hamiltonian

\[ H^{sl} = \xi \mathbf{s} \cdot \mathbf{L} \]

is added to the scalar-relativistic Hamiltonian \( H^0 \) after the self-consistent wavefunctions \( \psi_{i,k}^0 \) of \( H^0 \) are determined. The matrix elements \( H^{sl}_{ij} \) are calculated between states \( \psi_{i,k}^0 \) and \( \psi_{j,k}^0 \) at each \( k \) point and new wavefunctions are obtained from the diagonalization of the eigenvalue equation

\[ (H^0 + \xi \mathbf{s} \cdot \mathbf{L})\psi_{j,k} = \epsilon_{j,k} \psi_{j,k} \]

The X-ray absorption in the dipole-approximation is calculated by Fermi's golden rule using the new wavefunctions

\[ \sigma_\lambda(\omega) = \frac{2\pi}{\hbar} \int d\mathbf{k} \sum_i \left| \langle \psi_i | \epsilon_\lambda \cdot \mathbf{p} | \psi_{i,k} \rangle \right|^2 \delta(\epsilon_{i,k} - \epsilon_\lambda - \hbar \omega) \left[ 1 - f(\epsilon_{i,k}) \right] \]

where \( \epsilon_\lambda \) is the photon polarization vector (\( \lambda = \pm 0 \)) and \( f(\epsilon_{i,k}) \) is Fermi-Dirac function. \( \psi_i \) and \( \epsilon_i \) are the core state wavefunction and energy, respectively. For K-edge MCXD, the core state is 1s. According to the \( \Delta l = \pm 1 \) selection rule, only the \( p \) component in the valence states has non-zero contribution to the transition matrix elements. In our calculations, core-hole interactions are neglected since it is known that for K-edge spectra in d-electron systems, this approximation is a fairly good one [15]. A Lorentzian broadening of about 1.0 eV is employed to simulate the line width of excited states followed by 0.5 eV Gaussian broadening to simulate the experimental resolution. For the Fe-Ni alloys, a supercell geometry is employed.

The calculated MCXD and XANE spectra for bcc Fe, fcc Ni and fcc Fe/Ni(001) (to simulate Fe_{25}Ni_{75}) systems are shown in Figures 2 and 3. In the notation used here Fe/Ni(001) means a Fe-Ni superlattice with one layer of Fe and one layer of Ni grown alternately along the (001) direction on fcc lattice. Compared with Figs. 1, the calculations reproduce the main characteristics in the measured spectra up to near 30 eV above the edge. For the MCXD of bcc Fe, the theory gives four positive peaks at the edge and at about 10, 18 and 29 eV, and a main negative peak around 5 eV, in agreement with the experiment. For fcc Ni, the calculated MCXD shows three negative peaks at about 1, 4.5 and 9.5 eV, as observed in the measurements. In Fe/Ni(001), the calculations indicate a dramatic change in the Ni MCXD with the presence of Fe: a small negative peak followed immediately by a positive peak appears right at the absorption edge. However, the experiment shows only a positive peak at the edge in the Fe_{25}Ni_{75} alloy and it is about 1 eV lower than the theoretical one. This discrepancy may be due to the disorder of local symmetry and composition in the alloy not treated in the simulation.

To investigate the effect of symmetry and composition on the K-edge MCXD in the Fe-Ni alloy, we have calculated the MCXD and XANE's spectra for Fe/Ni(111) and Fe_{25}Ni(111) systems. The
results are also plotted in Fig. 2. Compared with Fe, the Ni MCXD is more sensitive to the crystal structure due to the fact that the Ni 4p wave functions are more extended. As shown in Fig. 2, the Ni MCXD spectra in Fe/Ni(111) and Fe/Ni(111) have different characteristic structures from that in fcc Ni or Fe/Ni(001). Note that only Fe/Ni(001) exhibits a positive peak near the edge, which implies that Fe-Ni alloys have fourfold symmetry. In the 3d transition metals, because the 3d valence states are more localized than the 4p's, the K-edge MCXD is more element, structure and composition specific than the L-edge. Therefore, it is possible to use the K-edge MCXD to probe the crystal structure by comparing experiments and theoretical calculations for different geometries.

Finally, we point out that in the energy region near the edge, the K-edge MCXD measures the 4p orbital polarization as a function of energy, or the difference of the 4p component in the density of states (p-DOS) between m_z=1 and m_z=-1 in the unoccupied states. To see this, we approximate the wave functions of the low energy valence states by the atomic valence orbitals in the vicinity of the nuclei

$$\psi_{i,k} = \sum_{lm} c_{lm}(i,k) R_i(r) Y_{lm}(\theta, \phi)$$

where $R_i$, with $i=1, 2, 3, \ldots$ are the atomic radius wave functions for the 4s, 4p, 3d, ... states, respectively, and $c_{lm}$ is the expansion coefficient. Substituting $\psi_{i,k}$ in Eq. 3 by Eq. 4 we have

$$\sigma_-(\omega) - \sigma_-(\omega) = A \int d\mathbf{k} \sum_{l \neq 0} \left( |c_{l,1}(i,k)|^2 - |c_{l,-1}(i,k)|^2 \right) \delta(\epsilon_{i,k} - \epsilon_c - \hbar \omega) \left[ 1 - f(\epsilon_{i,k}) \right]$$

with

$$A = -\frac{2\pi}{3\hbar} \int R_i \left( \frac{d}{dr} + \frac{2}{r} \right) R_i r^2 dr$$

where $R_i$ is the 1_core radius wave function. The right-hand side of Eq. 5 gives the 4p orbital momentum density, or the p-DOS difference at energy. The correspondence between the MCXD and the DOS
is illustrated in Fig. 3, where we plot the unoccupied $p$-DOS difference between $m = 1$ and $m' = -1$ (with a 0.8 eV Gaussian broadening) together with the MCXD (all normalized) for bcc Fe and fcc Ni. Clearly, these two curves have the same overall structure; the discrepancy is probably due to the different broadening employed in the two cases. These results demonstrate that the K-edge MCXD technique can be employed to detect the $4p$ electronic structure and polarization in transition metal systems.

CONCLUSIONS

In summary, we have examined the composition dependence of the MCXD spectra at both the Fe and Ni-edges in Fe-Ni alloys. The MCXD spectra reflect the itinerant character of the $4p$-electrons. The features of the MCXD spectra are sensitive to the crystal structure and composition of the alloys. The comparison with theoretical calculations shows that significant information can be obtained from the K-edge measurements on the $4p$-electronic structure and polarization in transition metal systems.

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