

## Orientation of the Ni magnetic moments in Ni–Zn ferrites

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### Abstract

We report the Ni  $L_{2,3}$ -edges magnetic circular dichroism measurements of the  $Zn_xNi_{1-x}Fe_2O_4$  ( $x = 0.0, 0.26, 0.50,$  and  $0.75$ ) ferrimagnet. The Ni average magnetic moments were found to decrease significantly with increasing Zn content. This observation is interpreted in terms of the Yafet–Kittel type canting of the Ni magnetic moment and shows values greater than those of the Fe magnetic moment determined from Mössbauer and neutron diffraction measurements. This work provides new information on the effect of Zn doping of Ni–O–Ni and Fe–O–Fe superexchange couplings.

$Zn_xNi_{1-x}Fe_2O_4$  is a ferrimagnetic compound which exhibits interesting doping-dependent magnetic properties. The saturation magnetization and the Néel temperature were found to change with Zn content; and a Yafet–Kittel (Y–K) type canting of the local Fe magnetic moments has been proposed to account for these observations [1, 2]. Due to the lack of Ni-specific magnetic measurements, however, the role of  $Ni^{2+}$  ions in the magnetic properties of the Ni–Zn ferrites is still not understood. For example, whether the Ni magnetic moments have a Y–K type canting similar to that of Fe magnetic moments, and how the Fe–O–Fe and Ni–O–Ni superexchange couplings are modified upon Zn doping remain as interesting open questions. To help reveal the role of the  $Ni^{2+}$  ions in this magnetic system, soft-X-ray magnetic circular dichroism (MCD) measurements at the Ni  $L_{2,3}$ -edges were conducted.

The soft-X-ray MCD measurements were performed at the AT&T Bell Laboratories Dragon beamline at the

National Synchrotron Light Source [3] using the fluorescence yield X-ray absorption spectroscopic (XAS) technique. The sample preparation, X-ray diffraction, and the chemical analysis of the  $Zn_xNi_{1-x}Fe_2O_4$  samples used in this study have been described elsewhere [4]. To facilitate MCD measurements, the samples were ground and sieved to fine powders, and then rubbed onto an adhesive type which was kept at room temperature.

Fig. 1 shows the photon-flux-normalized Ni  $L_{2,3}$ -edges XAS and MCD spectra of  $Zn_{0.5}Ni_{0.5}Fe_2O_4$ . The  $I_+$  ( $I_-$ ) is the absorption spectrum taken with the projection of the spin of the incident photons parallel (anti-parallel) to the spin direction of the Ni 3d majority electrons. The two white line regions, labeled as  $L_3$  and  $L_2$  in the top panel, are the electron transitions from the Ni  $2p_{3/2}$  and  $2p_{1/2}$  core levels to the Ni 3d unoccupied states, respectively [5, 6]. The MCD spectrum, e.g.  $I_+ - I_-$ , is shown in the bottom panel. Unlike the case of solid element nickel [5], rather complicated XAS and MCD spectra were observed, exhibiting strong multiplet and crystal field effects [6]. The lineshapes of the XAS and MCD

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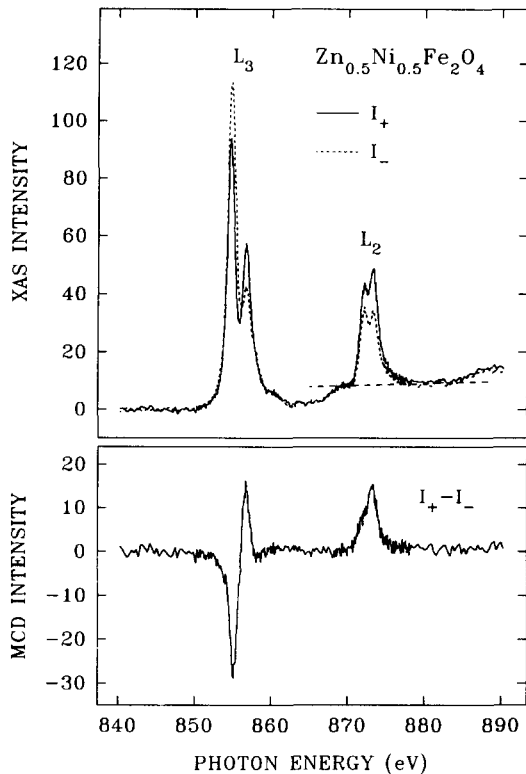


Fig. 1. Ni  $L_{2,3}$ -edges fluorescence yield X-ray absorption (XAS) and magnetic circular dichroism (MCD) spectra of  $Zn_{0.5}Ni_{0.5}Fe_2O_4$ .

spectra of  $x = 0, 0.26$ , and  $0.75$  samples were found to be nearly identical to those of the  $x = 0.5$  sample, except for their MCD asymmetry ratio, i.e.  $(I_+ - I_-)/(I_+ + I_-)$ . Since the MCD asymmetry ratio is proportional to the magnetic moment averaged over different sites and magnetic orientations, a quantitative evaluation of the asymmetry ratio can provide direct information on the Ni relative average magnetic moment as a function of Zn content. Among the various spectral regions from which one can calculate the asymmetry ratio, the  $L_2$  white line region is the best choice. This is because the main peak at  $\sim 855$  eV in the  $L_3$  white line region suffers seriously from self-absorption and saturation artifacts due to its large absorption cross-section; it is also very difficult to isolate the positive MCD signal of the satellite peak at  $\sim 857$  eV from the negative MCD signal of the main peak. After the removal of a linear background from the  $L_2$  white line (see the dashed straight line in Fig. 1), the XAS intensities between 870.9 and 875.6 eV were integrated separately for  $I_+$  and  $I_-$  spectrum. The asymmetry ratios thus obtained are 0.2241, 0.2241, 0.1926, and 0.1413 for the  $x = 0, 0.26, 0.5$ , and  $0.75$  samples,

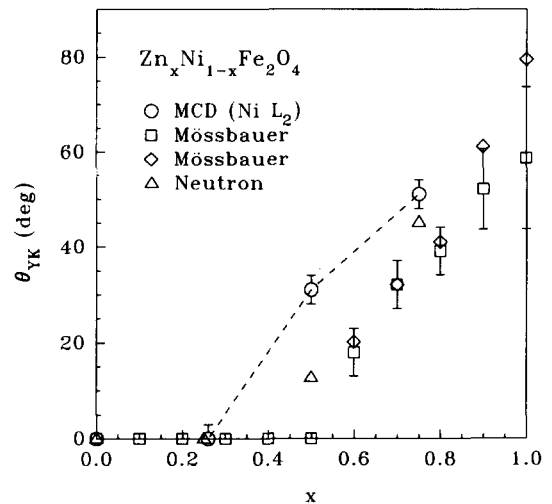


Fig. 2. Yafet-Kittel canting angles,  $\theta_{YK}$ , as a function of Zn content,  $x$ , from different magnetic measurements of  $Zn_xNi_{1-x}Fe_2O_4$ . The dashed line serves only as a guide to the eyes for the MCD data.

respectively, showing a progressive reduction of the Ni average magnetic moment with Zn doping over a certain threshold.

This phenomena can be interpreted as a non-collinear magnet moment arrangement proposed for Ni-Zn ferrites by Yafet and Kittel [7]. For simple ferrites such as  $MFe_2O_4$  ( $M = Mn, Co$ , and  $Ni$ ), the  $M$  substitutes the  $Fe^{3+}$  octahedral sites and leaves the  $Fe^{3+}$  octahedral sites intact. Regardless of whether the intra-sublattice coupling (between magnetic moments in octahedral and tetrahedral sites) is ferromagnetic or antiferromagnetic, the magnetic moments of  $M^{2+}$  or  $Fe^{3+}$  in the octahedral sites are parallel to one another, i.e. collinear, just as the magnetic moments in the  $Fe^{3+}$  tetrahedral sites are [8]. Upon Zn doping of the  $NiFe_2O_4$ , however, Yafet and Kittel proposed that a splitting of the octahedral-site into two subsites occurs, making the magnetic moments in the two subsites equal in magnitude but canted by an angle of  $\theta_{YK}$  with respect to the direction of their combined moment. The resultant combined magnetic moment of the octahedral subsites ( $Fe^{3+}$  or  $Ni^{2+}$ ) is still collinear with, but antiparallel to, that of the tetrahedral  $Fe^{3+}$  sites. By adopting this interpretation, we can relate the observed reduction of the average Ni moments to an increase in  $\theta_{YK}$ . If we assume that  $\theta_{YK} = 0$  for  $x = 0$ , then  $\theta_{YK}$  for any  $x$  can be calculated as  $\theta_{YK}(x) = \cos^{-1}(\text{asy}(x)/\text{asy}(0))$ , where  $\text{asy}(x)$  is the aforementioned MCD asymmetry ratio. The  $\theta_{YK}$  of the Ni magnetic moments thus determined are  $0^\circ, 0^\circ, 31^\circ$ , and  $51^\circ$  for  $x = 0, 0.26, 0.5$ , and  $0.75$  samples, respectively.

Fig. 2 compares the  $\theta_{\text{YK}}$  of the Ni moment determined from our MCD measurements with those obtained from neutron diffraction [1] and Mössbauer [2] measurements. Since the Mössbauer technique measures only the Fe moments, the  $\theta_{\text{YK}}$  thus determined are attributed to the Y–K canting of the Fe moments. The  $\theta_{\text{YK}}$  versus  $x$  plot of the Ni moment exhibits similar characteristics to that of the Fe moment, i.e. a monotonic increase in  $\theta_{\text{YK}}$  for Zn content above a threshold value, thus demonstrating that the Y–K type canting also occurs for the Ni magnetic moments. More interestingly, the threshold Zn content for the Ni moments seems to be lower than that for the Fe moments, and the  $\theta_{\text{YK}}$  are larger for Ni than for Fe. Considering that the Mössbauer data were taken at 7 K, these differences are even more pronounced. This clearly suggests that the influence of Zn doping on the

superexchange coupling is different for Ni–O–Ni as compared to Fe–O–Fe.

## References

- [1] N.S. Satya Murthy et al., *Phys. Rev. B* 181 (1969) 969.
- [2] L.K. Leung et al., *Phys. Rev. B* 8 (1973) 29.
- [3] C.T. Chen, *Rev. Sci. Instrum.* 63 (1992) 1229 and references therein.
- [4] T.M. Uen and P.K. Tseng, *Phys. Rev. B* 25 (1982) 1848.
- [5] C.T. Chen et al., *Phys. Rev. B* 42 (1990) 7262; *B* 43 (1991) 6785.
- [6] G. van der Laan and B. T. Thole, *Phys. Rev. B* 43 (1991) 13401.
- [7] Y. Yafet and C. Kittel, *Phys. Rev.* 87 (1952) 290.
- [8] L. Néel, *Ann. Phys.* 3 (1948) 137.