

Neutron Diffraction and Extended X-ray Absorption Fine Structure Studies of $\text{Pr}_3(\text{Fe}_{1-x}\text{Co}_x)_{27.5}\text{Ti}_{1.5}$ Permanent Magnet Compounds

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Abstract— Neutron diffraction (ND) and extended x-ray absorption fine structure (EXAFS) measurements were carried out to determine the long-range and short-range structural properties of Co-substituted $\text{Pr}_3\text{Fe}_{1-x}\text{Co}_x\text{Ti}_{1.5}$ compounds. ND refinement analysis indicates Ti atoms occupy the 4g and 4i Fe sites and Co atoms occupy, without preference, those Fe sites not shared with the Ti atoms. EXAFS measurements show the local environment of the Pr experiences increasing static disorder with the introduction of Co, and its coordination sphere contracts in the vicinity of those Co near neighbors. The Fe local environment remains unaffected with the introduction of Co suggesting that substitution in excess of 40% can be achieved in this structure.

Index Terms—extended x-ray absorption fine structure, neutron diffraction, Permanent magnets

I. INTRODUCTION

IN recent years there has been considerable interest in the synthesis of $\text{R}_3(\text{Fe},\text{M})_{29}$ (where R= rare earths; M = Ti, V, Mo, Cr, or Mn) compounds and their nitrides motivated in part by their potential as permanent magnets. For the case of $\text{Pr}_3\text{Fe}_{27.5}\text{Ti}_{1.5}$, Shah et al.[1] have shown that substitution of up to 30% Co for Fe increases the Curie temperature (T_C) by over 400 K making this compound a possible magnet for high temperature applications. The increase in T_C (and M_S) have been explained by these authors in terms of a preferential occupation of Co on those Fe sites that are believed to be antiferromagnetically coupled to other 3d lattice sites. To elucidate the effect of Co substitution on the 3:29 structure, and to establish the site occupancy of Co and Ti atoms, a combined study of the long-range and short-range structure has been carried out using neutron diffraction (ND) and extended x-ray absorption fine structure (EXAFS) measurements.

II. EXPERIMENTAL

The alloys whose properties are reported here were prepared by arc-melting the constituent elements and homogenizing the resulting ingot at temperatures up to 1200 °C. Further details of the processing, structure, and magnetic

properties of similarly prepared compounds are provided in ref. [1].

Neutron powder diffraction intensity data were collected using the BT-1 high-resolution diffractometer located at the reactor of the NIST Center for Neutron Research. A Cu (311) monochromator was employed to produce a monochromatic neutron beam of wavelength 1.5401(1) Å. Collimators with horizontal divergences of 15', 20', and 7' of arc full width at half maximum were used before and after the monochromator, and after the sample, respectively. The intensities were measured in steps of 0.05° in the 2θ range 3°-168°. Data were collected at room temperature for all samples. The structure refinements were carried out via the Rietveld fitting method using the program GSAS[2].

Extended x-ray absorption fine structure (EXAFS) data were collected in transmission mode under ambient conditions using the Naval Research Laboratory's beamline X23B at the National Synchrotron Light Source. Samples consisted of multiple layers of powder-impregnated tape that allowed tailoring of the absorption at the different edges. The extended fine structure were analyzed using standard procedural steps[3] leading to the element-specific Fourier transformation of the data to radial coordinates.

III. RESULTS AND DISCUSSION

A. Neutron Diffraction

The compounds studied here exist in the monoclinic ($A2/m$) space group.[4, 5] Figure 1 is a room temperature plot of the powder diffraction intensity data and the best fit provided by the GSAS refinement programs for the nominal $x=0.1$ compound. A difference plot is provided in Fig. 1 to aid the reader in determining the quality of fit. The signal-to-noise characteristics of the raw data and the quality of fit are representative of the other compounds studied here. The site distribution of the constituent elements in these compounds are summarized in Table I for $x=0.1$.

From the GSAS fitting of the $x=0$ alloy, we have deduced that the Ti atoms reside on the Fe3 (4g), Fe6 (4i) and Fe7 (4i) sites in percentages of 17.8%, 30.5%, and 23.9%, respectively. These are in agreement with the results of Yelon et al. [6] who, using ND reported for the Nd-containing 3:29 compound, found that Ti atoms distribute on these same sites with occupancies of 10.3%, 30.5% and 21.4%, respectively. The fitting of the Co-substituted compounds was performed by constraining the Ti-site distribution to that determined for the Co-free compound.

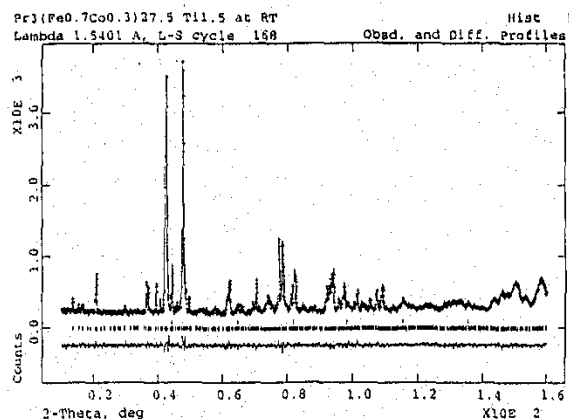


Figure 1. Powder neutron diffraction data for the $x=0.1$ compound shown with best fit provided by GSAS and the difference of the two data sets (see text for details).

Table I
Atom positions and site filling characteristics of all atom types determined by neutron diffraction of $\text{Pr}_3(\text{Fe}_{1-x}\text{Co}_x)_{27.5}\text{Ti}_{1.5}$ $x=0.10$

Atom Type	designation	Site	fractional occupancy	atomic positions		
				X	Y	Z
Pr	Pr1	2a	1	0	0	0
Pr	Pr2	4i	1	.401	0	.815
Fe	Fe1	2c	.851	.5	0	.5
Fe	Fe2	4e	.792	0	.25	.25
Fe	Fe3	4g	.806	0	.357	0
Fe	Fe4	4i	.795	.108	0	.723
Fe	Fe5	4i	.783	.291	0	.096
Fe	Fe6	4i	.653	.254	0	.525
Fe	Fe7	4i	.709	.142	0	.290
Fe	Fe8	8j	.833	.624	.147	.685
Fe	Fe9	8j	.775	.803	.218	.090
Fe	Fe10	8j	.798	.406	.252	.065
Fe	Fe11	8j	.804	.201	.252	.157
Ti	Ti1(Fe3)	4g	.194	0	.357	0
Ti	Ti2 (Fe6)	4i	.347	.254	0	.525
Ti	Ti3 (Fe7)	4i	.291	.142	0	.290
Co	Co1	2c	.149	.5	0	.5
Co	Co2	4e	.208	0	.25	.25
Co	Co3	4g	0	0	.357	0
Co	Co4	4i	.205	.108	0	.723
Co	Co5	4i	.217	.291	0	.096
Co	Co6	4i	0	.254	0	.525
Co	Co7	4i	0	.142	0	.290
Co	Co8	8j	.167	.624	.147	.685
Co	Co9	8j	.226	.803	.218	.090
Co	Co10	8j	.202	.406	.252	.065
Co	Co11	8j	.196	.201	.252	.157

This was done to improve the statistical sensitivity of the fitting analysis and was confirmed to be a valid assumption from analysis of the Ti K-edge EXAFS. The Co was found to distribute without preference on those Fe sites *not* shared with Ti. For the $x=0.1$ sample, no occupation of the Ti-shared Fe sites were measured, while for $x=0.3$ Co fills the Fe1, Fe2, Fe4, Fe5, and Fe9 sites at 30-40% occupancy and the Fe3, Fe6, and Fe7 (i.e. Ti-shared Fe sites) at 10-15% occupancy. From these trends it appears that the site occupancy of Co is determined in part by local strain fields created by the Ti filling of the 4g and 4i sites.

In addition to determining the site occupancy of the constituent elements in these compounds, the actual composition of the primary phase and weight fraction of detected phases were determined (see Table II). A residual α -Fe phase ranging from 1.5 - 9 wt-% was measured. The presence of metallic Fe is attributed to the loss of the Pr to vaporization and/or oxidation during processing and not necessarily an intrinsic limit of this compound to Co

substitution. The calculated stoichiometry is shown to contain more Co than the nominal values suggesting that the body-centered cubic metallic phase does not contain much Co. This is substantiated by the measured lattice parameter of this phase, $\sim 2.88\text{\AA}$, which is slightly larger than bcc Fe and much larger than bcc CoFe alloys. The measured amount of Co in the 3:29 compound is also affected to the amount of the residual bcc Fe present.

Table II
Phase purity and composition results of ND measurements and analysis.

x nominal	x actual	Ti nominal	Ti actual	α -Fe (wt-%)
0	0	1.5	1.45	3.5
.1	.197	1.5	1.66	9
.3	.38	1.5	1.56	1.4

The lattice parameters and structural properties derived from the ND studies are presented in Table III. These values are similar to those determined by XRD refinement of similarly prepared samples of the same stoichiometry carried out by Shah et al.[1]. Small differences in these values ($\leq 0.05\%$ in unit cell volume and lattice parameters) can be attributed to several sources, including: differences in sample stoichiometry including residual phases present; diffractometer accuracy; and/or the details of the refinement analysis, for example, Co was omitted from the XRD refinement due to the inability of x-rays to differentiate between Co and Fe. Overall, one sees that the unit cell volume decreases $\sim 0.7\%$ with Co substitution over the range of $x=.1-.3$. Over this same substitutional range, the T_C increases by 400K [1] indicating that a magnetovolume effect on the 3d sublattice is not the dominant mechanism as was found to be the case in T_C enhancement by applied pressure [7] and nitrogenation [8]. Shah et al. proposed that the substitution of Co increases net exchange and T_C by reducing the negative contribution of antiferromagnetic coupled sites on the 3d sublattice. In accordance with the mechanism proposed by Shah et al., we find that the Co occupies those Fe sites (namely Fe1, Fe2, Fe4, Fe5, Fe8, Fe9) that they postulate are AF coupled sites. However, exchange modification arising from the contraction of the Pr coordination sphere may also contribute to the T_C enhancement.

TABLE III
Physical properties of Co-substituted $\text{Pr}_3(\text{Fe}_{1-x}\text{Co}_x)_{27.5}\text{Ti}_{1.5}$ compounds determined by neutron powder diffraction measurements.

Co content	a (\AA)	b (\AA)	c (\AA)	β (deg.)	u.c. volume (\AA^3)
0	10.655	8.606	9.757	96.951	888.2
0.1	10.637	8.606	9.767	96.758	887.9
0.3	10.610	8.585	9.750	96.703	882.1

B. EXAFS

The analysis of the Fourier transformed EXAFS data is limited to a qualitative analysis of the local environment around each element or to a quantitative analysis of the *average* environment around each element (not discussed here). This limitation arises from the large number of atomic correlations that contribute to the average near neighbor environment of each constituent that is measured by EXAFS. In order to describe the average environment quantitatively

one must float several adjustable parameters that compromises the statistical significance of the analysis.

The Pr L_{III} EXAFS study indicates an increase in isotropic atomic disorder around the Pr ions with the introduction of the Co substituent. A slight contraction of the NN <Pr-Fe/Co> bond is also evident for x=0.1 and x=0.3. This indicates that the decrease in unit cell volume measured by ND arises from a contraction of average Pr coordination sphere in response to the Co substitution.

In contrast, the Fourier transformed Fe K EXAFS (Fig. 2b) remain unchanged with increased Co substitution indicating the lack of local strain and/or disorder in the local environment of Fe. This indicates that the local distortion of the structure are localized at the Pr sites and are likely due to relaxation of the Pr bonds around the Co sites. Further, the lack of strain in the Fe environment suggests that a larger amount of Co may be accommodated by the 3d lattice in this structure.

Finally, the Fourier transformed Ti K EXAFS (Fig. 2c) shows no significant change in local symmetry with Co

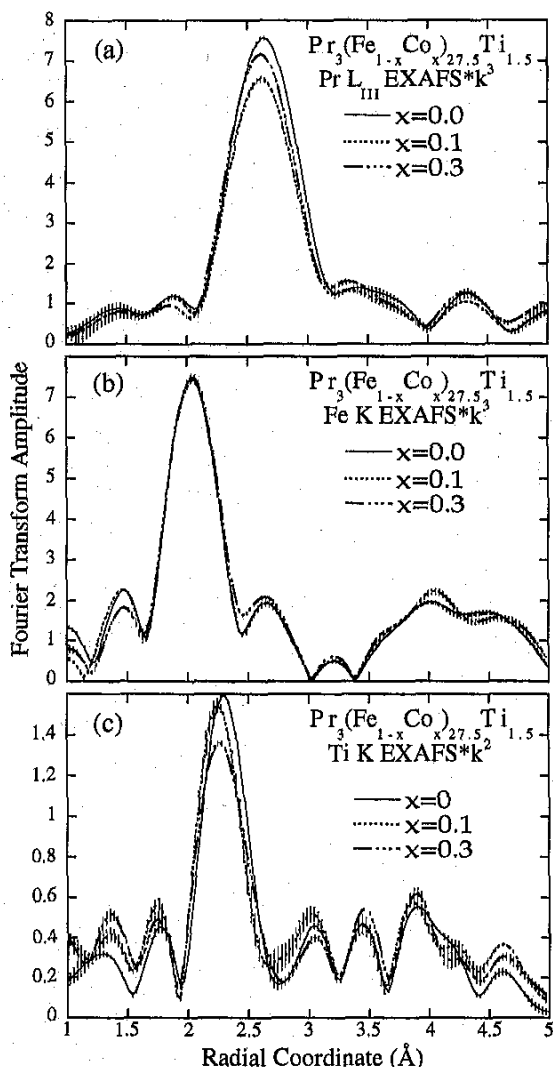


Figure 2. Fourier transformed Pr L_{III}, Fe K, and Ti K EXAFS for x=0, .1, and .3 compounds. Error bars on these plots reflect, both the data collection statistics and the uncertainty introduced to the data from the procedural steps leading to and including the Fourier transformation. k-ranges for panels a), b), and c) are: 2.9-10.9Å⁻¹, 3.3-12.2Å⁻¹, and 3-13.1Å⁻¹, respectively.

substitution. This supports the assumption employed in the ND analysis that Ti does not change site occupancy with the substitution of Co for Fe in this compound. Some disorder of the Ti near neighbor environment is observed in the x=.3 compound and corresponds to the shared occupancy of the 4g and 4i sites with Co. The limitation of Co substitution in this structure will likely be governed by Ti-Co interaction and not the Fe-Co or Pr-Co interactions.

IV. CONCLUSIONS

The following findings are deduced from the combined application of ND and EXAFS measurements to the Pr₃Fe_{1-x}Co_xTi_{1.5} compounds:

1. Ti atoms are confirmed to reside on the 4g and 4i Fe sites. This is consistent with ND studies of the Ti-substituted Nd-containing 3:29 compound[6]. EXAFS indicates that the Ti site occupation does not change appreciably with the substitution of Co.
2. Co atoms are found to occupy, without preference, those Fe sites not shared with Ti. These sites, including the Fe1, Fe2, Fe4, Fe5, Fe8, and Fe9, are the sites proposed by Shah et al. as possible AF coupled sites that would lead to an enhanced exchange and increased T_C.
3. Unit cell volume is measured to decrease ~0.7 % over the substitutional range of x= 0.0 - 0.3. EXAFS shows that the volume decrease is the result of a contraction of the Pr average coordination sphere in the vicinity of Co neighbors. This contraction of the Pr environment may effect the Pr-Fe exchange and possibly contribute to the T_C enhancement.
4. Fe EXAFS shows no signs of local strain in the 3d sublattice with increased Co substitution. This suggests that Co in excess of 40% may be incorporated into the Pr-containing 3:29 structure.

This study illustrates the value of combining a long-range structural probe with an element-specific short range structural probe to provide complimentary information. Either of these techniques used alone would not have provided a complete picture of the structure of these compounds.

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