NOTICE

CERTAIN DATA CONTAINED IN THIS DOCUMENT MAY BE DIFFICULT TO READ IN MICROFICHE PRODUCTS.

BNL--45147

DE91 001123

EXAFS Study of the Position of Zr within the Unit Cell of Sm_2Co_{17}

L. Rabenberg

Center for Materials Science and Engineering, The University of Texas at Austin, Austin, TX 78712

E.V. Barrera

Department of Mechanical Engineering and Materials Science, Rice University, Houston, TX 77251.

C.E. Maury and C. H. Allibert

Laboratoire de Thermodynamique et PhysicoChimie Métallurgiques, associé au Centre National de la Recherche Scientifique (Unite associé 29), ENSEEG, B. P. 75, 38402 St. Martin-d'Hères, France

S. M. Heald

Materials Science Division, Brookhaven National Laboratory, Upton, NY 11973

Extended X-ray Absorption Fine-Structure Spectroscopy (EXAFS) has been used to determine the position of Zr within the unit cell of Sm_2Co_{17}. Zr is routinely added to Sm_2Co_{17} permanent magnet alloys because of its effects on their metallurgical development, but the details of its behavior remain controversial. Induction melted Sm_2Co_{17}:Zr ternary alloys, aged at 1180 °C, then quenched, consisted of intimately mixed H2:17 and R2:17 having Zr in solid solution as well some regions of R2:17 that were poor in Zr. EXAFS spectroscopy of these specimens indicates that the most probable position for Zr is a site having two Sm near neighbor atoms and 11 Co atoms distributed over three different interatomic distances. This is consistent with a direct substitution of Zr for Co in the Co site in the mixed planes (12j in $P6_3/mmc$, or 18f in R3m). These results are discussed in terms of the metallurgy of 2:17 magnet alloys.

PACS numbers: 75.50. -y, 61.10.Lx, 81.20 Gx

INTRODUCTION

Permanent magnets based on Sm_2Co_{17} normally contain significant amounts of Fe and Cu as well as a small amount of Zr. In these alloys, the Fe raises the magnetization and Cu is believed to promote a uniform precipitation of $Sm(CoCu)_5$. Zr was originally introduced by Ojima *et al.*[1] who showed that energy products of 30 MGOe could be achieved with alloys of nominal composition $Sm(Co_{0.68}Fe_{0.21}Cu_{0.10}Zr_{0.01})_{7.4}$.

Zr is now routinely added to alloys of this type even though its behavior remains a matter of discussion.[2-8] Zr is reported to modify the high temperature stability of these alloys[3-5,9-12], participate in the development of the cellular microstructure[9], and increase the rate of chemical segregation of the Fe to the $Sm_2(CoFe)_{17}$ phase and Cu to the $Sm(CoCu)_5$ phase.[2] Most of the hypotheses regarding the metallurgical roles of Zr in Sm_2Co_{17}-based permanent magnets rest on assumptions concerning the crystallographic site(s) of the Zr atoms when dissolved in Sm_2Co_{17}.

It is possible to argue from indirect evidence that Zr occupies each of the several crystallographically inequivalent sites within the mixed planes of the Sm_2Co_{17} unit cell. From changes in magnetic properties and unit cell volume with Zr concentration, it has been argued[6,13] that Zr substitutes for Co, probably at the "dumbbell" positions (6c in R 2:17, or 4f in H 2:17). Based on atomic radii, variations of the c/a ratio, and correlations with the $Ce_2(CoFe)_{17}$ system, it has been argued[3] that each Zr enters a dumbbell along with a vacancy in preference to Fe-Fe pairs. However, Mössbauer results[14] directly contradict this idea. Precise determinations of the compositions of the 2:17 phases,[4] the details of the Sm-Zr-Co ternary phase diagram[10] and the vertical sections of the Sm-Zr-Co-Cu-Fe system[11] indicate that Zr substitutes for Sm. The fact that $ZrCo_2$ exists[15] and is isostructural with $SmCo_2$ argues that chemical interactions favor a substitution of Zr for Sm. Zr encourages the formation of the phases of the type $(SmZr)_{n+1}(Co)_{5n-1}$ in five-component permanent magnet compositions,[2,16] suggesting that Zr takes the mixed plane Co site of the 2:17 unit cell - the site that becomes a Sm site in the (n+1):(5n+1) phases.

It is the purpose of this article to report direct evidence based on Extended X-ray Absorption Fine Structure Spectroscopy (EXAFS) regarding the position of Zr in Sm_2Co_{17} unit cells. EXAFS probes the near-neighbor configurations of a specific chemical species within a volume of condensed matter;[17,18] as such, it is ideally suited to the direct experimental determination of the atomic configuration surrounding each Zr atom dissolved in Sm_2Co_{17}.

These results should eliminate one of the fundamental uncertainties in metallurgy of these permanent magnet alloy systems.

EXPERIMENTAL

Medium frequency induction was used to melt Sm ingots (purity 99.9%), electrolytic chips of Co (purity 99.99%) and Zr ribbons (purity 99%) together in a BN crucible under pure Ar before casting into a copper mold. Pieces of the cast ingot were wrapped in Mo foil, enclosed in a Mo cell, and heated by induction in a pure He atmosphere for 4 hours at 1180 °C. The rate of cooling following this homogenization treatment was approximately 300 °C per minute from 1180 °C to 850 °C; the He atmosphere was maintained throughout the quench. The composition of the specimens, $Sm_{10}Zr_2Co_{88}$ (atomic percent), was chosen as the composition near the center of the 2:17 (H) homogeneity range[10] at 1200 °C that would have adequate Zr for a strong EXAFS signal but not so much as to saturate the preferred sites.

Prior to EXAFS analysis, the sample was thoroughly characterized using optical microscopy, scanning electron microscopy (SEM) with energy dispersive x-ray microanalysis (EDS), x-ray powder diffractometry (XRD), and transmission electron microscopy (TEM).

EXAFS data from the Zr in the 2:17 samples were collected in the fluorescence mode usingbeamline X-11A at the National Synchrotron Light Source. A fluorescence ion chamber was used as the final detector, and yttrium oxide filters[18] were used to reduce the background fluorescence from Co and Sm. Data were acquired from an unoriented powdered 2:17 sample; then on subsequent runs, magnetically oriented samples were interrogated with the polarization vector of the synchrotron radiation being parallel to, then perpendicular to, the crystallographic c-axis.[19] The experimental data was analyzed by fitting the pre-edge and background and subtracting it to leave the normalized EXAFS oscillations. The EXAFS was then Fourier transformed, the first shell peak was selected, backtransformed to produce the single shell characteristic oscillatory wave form. The corrected chi data was then fit to theoretical spectra generated from models of the several sites, using the EXCURVE program.[20] In the EXCURVE program, the parameters[18] such as N_i (the number of neighbors in shell i), R_i (the distance from the target atom to shell i), σ_i (the Debye-Waller factor), and E_o (the edge value correction factor) are iterated until a calculated curve fits the experimental results. Transmission mode EXAFS from Zr and Co in thin-foil pure-metal standards was used to deduce the parameters used in the theoretical modelling.

RESULTS

The optical and scanning electron microscopy indicated that the sample was predominately 2:17 material containing Zr near the nominal concentration. Extensive searches of metallographic sections revealed (1) a very small quantity of Zr-rich particles along some of the grain boundaries and (2) a few larger regions containing essentially no Zr. EDS analysis indicated that the bulk of the Zr was in the matrix 2:17 material. XRD patterns were composed of peaks from hexagonal and rhombohedral 2:17 with no observable peaks from the Zr-rich phase. The lattice parameters of the 2:17 R are **a** = 0.8462 nm and **c** = 1.2254 nm, and those of the 2:17 H are **a** = 0.8462 nm and **c** = 0.8170 nm. The particles of Zr-rich material remain unidentified because they were too small for quantitative analysis by EDS in the SEM and they gave no specific peaks in the XRD pattern.

Transmission electron diffraction patterns from several areas of the specimen indicate an intimate mixture of R, H, and long period stackings. This suggests that the alloy is in an intermediate state in which there are microdomains with dumbbells stacked in hexagonal symmetry and microdomains with dumbbells stacked in rhombohedral symmetry. In all cases, the 2:17 reflections are streaked parallel to the $[0001]^*$ axis, but that they are not broadened in the other dimension, *i. e.* parallel to $[1010]^*$. This indicates that the arrangement of dumbbells within a given basal plane is very regular but that the correlation of one basal plan with another does not persist for more than a few unit cells. TEM images show some very small (~ 10 nm) domains with contrast typical of twinned rhombohedral 2:17 (two orientational variants); other areas show lattice fringes typical of higher order stacking sequences. Areas showing both of these types of contrast as well as areas with no contrast merge continuously into each other.

The data from the EXAFS of the unoriented sample (Figure 1) was very well modelled in terms of a substitution of Zr at a site similar to the mixed-plane Co site (12j site in H2:17). The best fit corresponds to 6 Co neighbors at 0.276 nm (cobalt -plane Co: σ = 2.1 pm), 3 Co neighbors at 0.263 nm (mixed plane Co: σ = 2.2 pm), 2 Sm neighbors at 0.266 nm (σ = 1.4 pm), and 2 Co neighbors at 0.306 nm (dumbbell Co: σ = 1.4 pm). In addition to the displacements about the mean positions as represented by the Debye-Waller factors, σ_i, a statistical variation of ± 4 pm in each interatomic distance is estimated. The fit between experiment and theory for Zr at the dumbbell site (4f in H2:17) was marginally acceptable; but was completely unacceptable for Zr in a Sm sites (2b and 2d in H2:17). Polarization-dependent data was necessary for complete discrimination between the mixed-plane Co site and the dumbbell site. When the polarization vector is parallel to the basal plane, $k^3\chi(k)$ curves

(Figure 2) indicate the presence of two different first shell neighbors as evidenced by the "beat" in the function at large k; when the polarization vector is parallel to c, no such beat is evident, indicating only one type of atomic neighbor. Because this behavior is consistent with the mixed plane Co site, but not the dumbbell site, it unambiguously indicates that the Zr in this sample is at the dumbbell site.

DISCUSSION

The SEM, TEM, and XRD observations are consistent with the idea that the bulk of the Zr was dissolved in the H2:17 phase at 1180 °C, but that a small amount of Zr-free R2:17, as well as a few particles of the Zr-rich phase were also present. During the quench, the H2:17 became unstable with respect to decomposition into R2:17, 1:5 and a Zr-rich phase. The quench was rapid enough to prevent long-range diffusion, but it did not completely prevent the local atomic rearrangements that convert H2:17 to R2:17. As a result, TEM investigations find evidence for microdomains of both R2:17 and H2:17. The Zr-rich particles and the regions that had been R2:17 at 1180 °C were retained to room temperature without significant changes.

The EXAFS signal is derived largely from Zr atoms trapped within the 2:17 material, and, because the 2:17 is in the process of transforming from one structural modification to another, the results may be open to some criticism. However, it must be recalled that (1) the transformation from H2:17 to R2:17 only involves a rearrangement of the dumbbells relative to each other and that (2) the dumbbells are separated from each other by 0.64 nm. The dumbbells are certainly not nearest neighbors in either structure. Since the EXAFS signal is derived primarily from nearest neighbor configurations, it is expected to be insensitive to the form of the 2:17 -- whether it is H or R, or whether it is in the process of transforming from one to the other.

The observation that Zr substitutes for Co in the mixed plane is consistent with the report[13] that the volume of the unit cell expands slightly, that the a-axis parameter expands significantly, and the c-axis parameter contracts slightly with Zr additions. The mixed plane Co site in pure Sm_2Co_{17} has two nearest neighbor Sm atoms at 0.282 nm, a separation that is considerably less than the sum of the atomic radii of Co and Sm. Substitution of an oversized atom like Zr at such a site should certainly result in an increase in unit cell volume in general and the a-axis parameter in particular.

These results are directly consistent with the observations[2,4,16] that Zr tends to stabilize phases similar to the Sm-rich (n+1):(5n+1) phases. The (n+1):(5n+1) phases are formed from the 1:5 structure by ordered substitutions of Sm for Co at the Co site in the mixed plane. If Zr

replaces Sm in this process, that is, if Zr systematically substitutes for Co in the mixed planes, ternary compounds having Bravais lattices similar to the (n+1):(5n+1) phases are formed. The platelet phase in commercial magnets is most probably such a phase.

Substitution of a strongly electropositive atom such as Zr at the mixed plane Co site can be expected to have significant effects on the contribution of the atoms in the adjacent dumbbell sites to the magnetocrystalline anisotropy as well as the tendancy of other elements to prefer the dumbbell sites. Thus, these results are not inconsistent with the report that Zr effects the magnetocrystalline anisotropy[6] nor are they inconsistent with the suggestion[3] that Zr prevents Fe from substituting at the dumbbell sites.

The results of this study are only partially consistent with the published phase diagram studies[4,10-12] which indicate that Zr expands the field of stability of 2:17 at high temperatures (~1200 °C) both in the direction of increasing Co at a constant Sm concentration and in the direction of increasing Sm at a constant Co concentration. The alloy used in these experiments had the same Sm content as does binary Sm_2Co_{17}, and the results are consistent with a simple substitution of Zr for Co. However, if the overall Co concentration had been held constant, the Zr would have had to either (1) substitute for Sm, (2) induce the structure to accept more dumbbells than are required for 2:17 stoichiometry as it occupied available Co sites in the mixed plane, or (3) cause an extensive rearrangement of atoms and sites within the unit cell. This study unfortunately cannot discriminate between these possiblities.

ACKNOWLEDGMENTS

L. Rabenberg gratefully acknowledges grants from the French Ministry of Research and from the University Research Institute of the University of Texas at Austin. Additional support for this research was provided by the US Department of Energy, Division of Materials Sciences, under contract #DE-AS05-80ER10742 and #DE-AC02-76CH00016.

1. T. Ojima, S. Tomizawa, T. Yoneyama, and T. Hori, IEEE Trans. Mag. **MAG-13**, 1317 (1977).

2. L. Rabenberg, R. K. Mishra, and G. Thomas, J. Appl. Phys. **53**, 2389 (1982).

3. A. E. Ray, Proceedings of the 1989 Annual Meeting of the Materials Research Society.

4. S. Derkaoui, C. H. Allibert, F. Delannay, and J. Laforest, J. Less-Common Metals, **136**, 75, (1987).

5. H. H. Stadelmaier, E.-Th. Henig, G. Schneider, and G. Petzow, *Z. Metallkunde* **79**, 313, (1988).

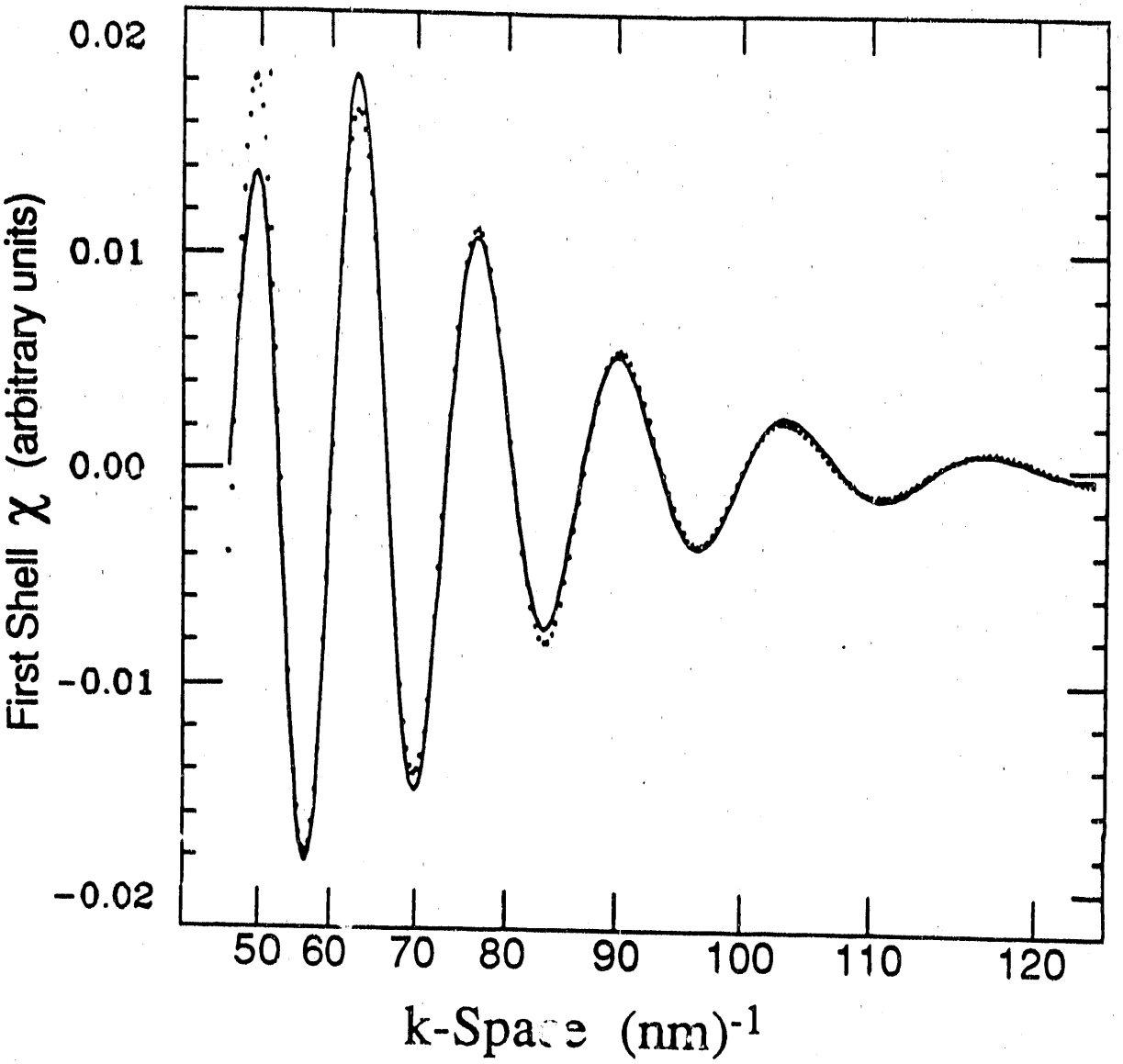
6. M.V. Satyanarayana, H. Fujii, and W.E. Wallace, J. Appl. Phys. **53**, 2374, (1982).

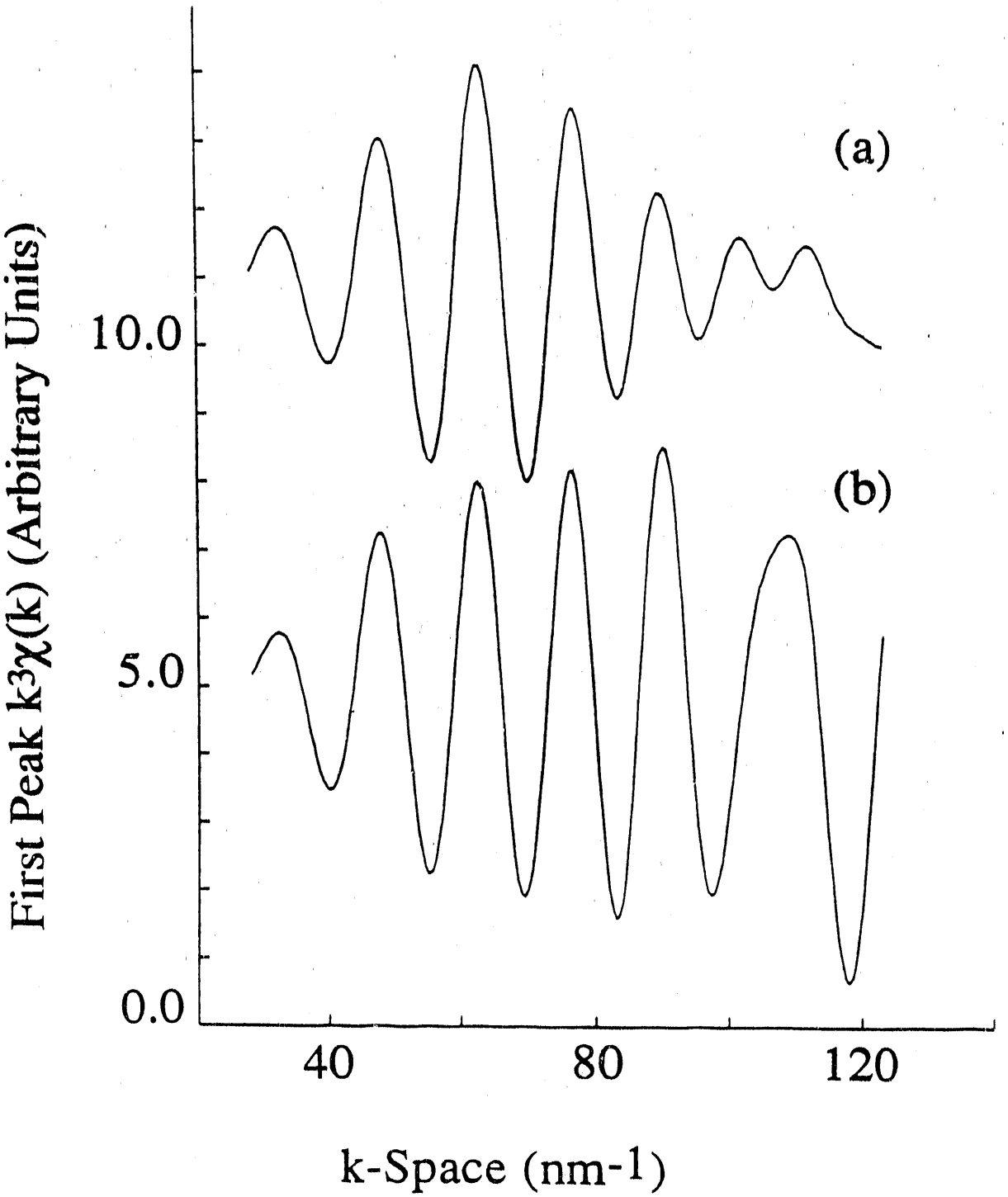
7. G.C. Hadjipanayis, R.C. Hazelton, K.R. Lawless, and L.S. Horton, IEEE Trans. Magn. **MAG-18**, 1460, (1982).
8. J. Fidler, P. Skalicky, and F. Rothwarf, IEEE Trans. Magn. **MAG-19**, 2041, (1983).
9. L. Rabenberg, R.K.Mishra, and G. Thomas, in J. Fidler, ed., Proc. 6th Int. Workshop on RE-Co Permanent Magnets, Technical University Vienna, (1982), p. 599.
10. T. Nishio, Y. Fukui, and Y. Iwama, J. Japan. Inst. Metals **52**, 502, (1988).
11. Y. Morita, T. Umeda, and Y. Kimura, IEEE Trans. Magn. **MAG-23**, 2703, (1987).
12. T. S. Chin, W. C. Chang, R. T. Chang, M. P. Hung, and H. T. Lee, IEEE Trans. Magn. **25**, 3782, (1989).
13. H. Fujii, M.V. Satyanarayana, and W.E. Wallace, Solid State Comm. **41**, 445, (1982).
14. Ma Ruzhang, Li Zhengwen, Ping Jueyun, Feng Yongrong, and Pan Shuming, Proc. 7th Int. Workshop on RE-Co Permanent Magnets, X. Pan, W. Ho, and C. Yu, eds., Beijing, (1983), p. 373.
15. W.H. Pechin, D.E. Williams, and W.L. Larsen, Trans. TMS-AIME **57**, 464, (1964).
16. F. Delannay, S. Derkaoui, and C.H. Allibert, J. Less-Common Metals **134**, 249, (1987).
17. E. A. Stern and S. M. Heald, in Handbook on Synchrotron Radiation E. E. Koch, ed. (North-Holland, Amsterdam, 1983) Vol. 1 p.955ff.
18. P. A. Lee, P. H. Citrin, P. Eisenberger, and B. M. Kincaid, Rev. Mod. Phys. **53**, 769, (1981).
19. J. L. Feldman, W. T. Elam, A. C. Ehrlich, E. F. Skelton, and D. D. Dominguez, Phys. Rev. B33, 7961, (1986).
20. N. Binsted, S. J. Gurman, J. W. Campbell, EXCURVE 88 Program, SERC Danbury Lab. (1988).

FIGURE CAPTIONS

Figure 1. Experimental and theoretical EXAFS data $\chi(k)$ from the unoriented sample. The solid line is the actual experimental data; the dotted line represents the best modelling of the data from the EXCURVE program with Zr at a mixed-plane Co site.

Figure 2. Experimental EXAFS data weighted by k^3 [$k^3\chi(k)$]comparing the signal from (a) a sample with its c-axis parallel to the polarization vector with (b) a sample oriented with its c-axis perpendicular to the polarization vector. The "beat" in curve (b) at high k is characteristic of the presence of two dissimilar atoms in the first shell.


0.02
0.01
0.00
-0.01
-0.02
First Shell χ (arbitrary units)
50
60
70
80
90
100
110
120
k-Space (nm)-1


First Peak k3χ(k) (Arbitrary Units)
10.0
5.0
0.0
(a)
(b)
40
80
120
k-Space (nm-1)

-END-

DATE FILMED

11/05/90