XAFS Study of the Local Structure of *a*-Gd_xSi_{1-x} Magnetic Semiconductors

D. Haskel,[1] J. O. Cross,[2] J. W. Freeland,[1] R. Winarski,[1] M. Newville,[3] S. W. Han,[4] B. L. Zink,[5] F. Hellman[5]

[1] *Advanced Photon Source (SRI-CAT), Argonne National Laboratory, Argonne, IL, U.S.A.*

[2] *University of Washington and Advanced Photon Source (PNC-CAT), Argonne National Laboratory, Argonne, IL, U.S.A.*

[3] *University of Chicago and Advanced Photon Source (GEO-CARS), Argonne National Laboratory, Argonne, IL, U.S.A.*

[4] *Department of Physics, University of Washington, Seattle, WA, U.S.A.*

[5] *Department of Physics, University of California, San Diego, CA, U.S.A.*

Introduction

Amorphous magnetic semiconductors provide an excellent framework for studying the effect of local magnetic moments on transport properties in the presence of disorder. It was recently demonstrated in *a*-Gd_xSi_{1-x} that the interaction between localized moments and conduction electrons leads to strong carrier localization at low temperatures in zero field but results in large negative magneto-resistance in the presence of a magnetic field.[1] The enhanced localization is attributed to the exchange interaction between conduction electrons and randomly oriented local moments, which increases the effective mass of the carriers.[1] Understanding the competition among disorder, magnetic effects (polarization of conduction electrons by localized moments), and Coulomb effects (electron-electron interactions) may also provide insight into the similar physics that occurs in colssal magneto-resistance and high-T_c superconductors. Structural characterization of these alloys is obviously important.

The interaction between Gd moments is mediated by the conduction electrons, and its details depend on how the localization length or elastic mean free path compares with the Gd-Gd interatomic distance. Volume effects can also be important, particularly in the vicinity of a metal-insulator transition. Here we report on x-ray absorption fine structure (XAFS) measurements at the Gd L_3 and Si K-edges of these amorphous binary alloys. XAFS is ideal for the study of amorphous materials since it does not require crystalline order. In addition, it is element-specific; i.e., it determines *partial* pair distribution functions between the absorber and its neighbors. Other techniques measure a sum over all pair correlations, which includes only a small contribution from the dilute dopants.

Experimental

Experiments were performed at Sector 20 (PNC-CAT) and Sector 2 (SRI-CAT). Samples used in this study were coevaporated from Si and Gd sources onto amorphous silicon-nitride-coated Si substrates.[1] Samples with Gd concentrations of 4, 7, 12 and 18 at. % were studied. Gd L_3 edge measurements were performed in fluorescence using a single-element Ge solid state detector. The measurements were done at T ≅ 12 K to reduce thermal vibrations, which decrease the XAFS amplitude. For Si K-edge measurements, samples were sputtered *in situ* until the near-edge region showed no indication of the presence of an oxide surface layer; data were collected in the total electron yield mode.

Results and Discussion

Figure 1 shows the magnitude of the complex Fourier transform of the XAFS at the Gd L_3 edge of a x=0.18 sample (top panel) together, with that for a Gd metal foil (bottom panel). The first peak in the Fourier transform (F.T.) is related to the pair distribution function of Gd and its first neighboring atoms. Structural parameters were derived from the data by a nonlinear least squares refinement of theoretical standards from FEFF6.[2] We found that Gd is surrounded by Si atoms, coordination number N=4.8±1.0, at a distance of 3.00(3) Å. These values are the same, within uncertainties, for all four samples. We found no evidence for Gd clustering or Gd nearest neighbors up to x=0.18, consistent with the theoretical expectation for a solid solution at these nominal Gd concentrations. For comparison, the F.T. of Gd metal foil is shown in the bottom of Fig. 1; its refined nearest neighboring distance is 3.550(8) Å. Besides the important result of verifying the solid solution nature of the alloy, our measurements indicate a significant local expansion of the Si network around the Gd dopants (the Si-Si distance in crystalline Si is 2.35 Å). Figure 2 shows XAFS results obtained at the Si K-edge. We found that Si is surrounded by Si (coordination N=3.7±0.3) at a mean distance of 2.390(8) Å. The variation in these numbers for the different Gd concentrations studied is smaller than their uncertainties. The mean squared disorder in Si-Si distance systematically increases

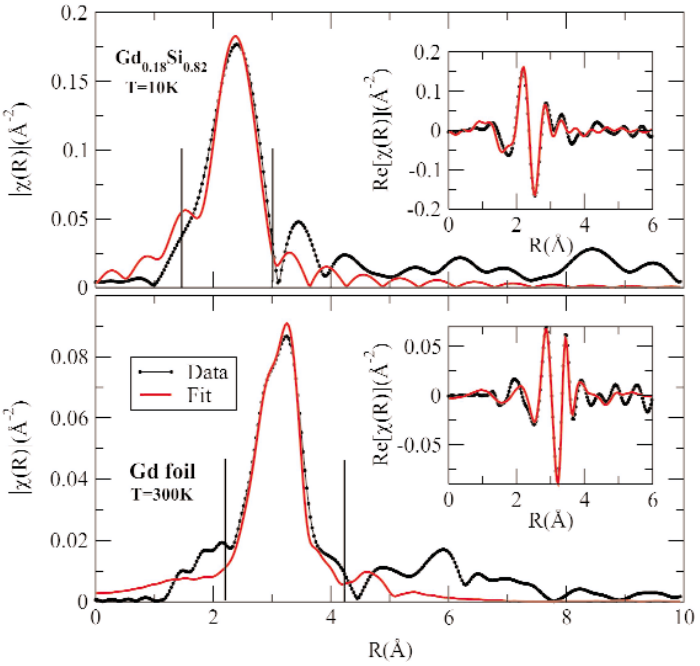

FIG. 1. Magnitude of the complex Fourier transform of the XAFS signal at the Gd L_3 edge of a x=0.18 sample (top) and for a Gd metal foil (bottom). The vertical lines show the region of real space fitted. The insets show the real part of the complex Fourier transform.

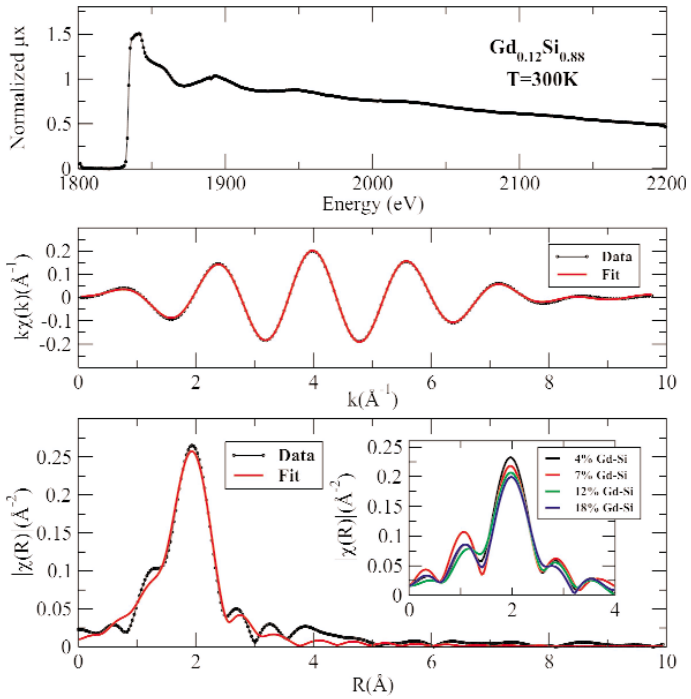

FIG. 2. Normalized absorption (top), first shell XAFS (middle), and real- space data and fits at the Si K-edge of a x=0.12 sample. The inset in the lower panel show the reduction in first shell amplitude as the Gd concentration increases.

with concentration of Gd. This disorder varies from 0.0048(9) Å^2 at x=0.04 to 0.008(1) Å^2 at x=0.18. This increase results in a decrease of the first shell XAFS amplitude with Gd concentration, as shown in the inset of the lower panel of Fig. 2. This is not surprising since Gd locally expands its immediate surroundings and the Si network becomes progressively distorted to accommodate the increased strain. We note, however, that despite the large Gd concentration at x=0.18, the overall increase in disorder is not large in an absolute scale: this is about the increase expected in a crystalline material due to thermal vibrations in a 10-300 K temperature range. The amorphous network then acts quite efficiently in accommodating the local strain introduced with Gd. It is interesting to note that despite the large local expansion around Gd atoms, 0.65 Å relative to crystalline Si, the average amorphous Si network does not significantly expand but becomes slightly more disordered. The strain field around the dopant is therefore largely confined to its first nearest neighbor environment.

Summary

We have confirmed the solid-solution characteristics of the Gd_xSi_{1-x} system using a local structural probe. We found a large local expansion of the Si-Si network around a Gd dopant (0.65 Å relative to crystalline Si). This local expansion is responsible for an increased disorder in the Si network as the Gd concentration is increased. On an absolute scale, the increased disorder is quite small, indicating an ability of the amorphous network to efficiently accommodate the local strain. The average Si-Si distance in these amorphous alloys is 0.04 Å longer than in crystalline Si.

Acknowledgments

We thank D. Brewe, S. Heald, and E. Stern for valuable contributions. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

References

[1] F. Hellman, M.Q. Tran, A.E. Gebala, E.M. Wilcox and R.C. Dynes, Phys. Rev. Lett. **77**, 4652 (1996); F. Hellman, D.R. Queen, R.M. Potok and B.L. Zink, Phys.Rev. Lett. **84**, 5411 (2000).

[2] S. Zabinsky, J.J. Rehr, A. Ankudinov, R.C. Albers and M.J. Eller, Phys. Rev. B **52**, 2995 (1995).