XAFS Examination of Mn Local Structure in $Ga_{1-x}Mn_xAs$ and $Ga_{1-x-y}Mn_xBe_yAs$

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Introduction

One recent topic of interest in materials science/condensed matter physics has been a group of systems known as "spintronic" materials. These materials are semiconductors with magnetic moments; thus, their electrical properties are coupled with magnetic moments. Both materials of this investigation, $Ga_{1-x}Mn_xAs$ and $Ga_{1-x-y}Mn_xBe_yAs$, are from this group. The Mn added to the GaAs provides magnetic moments and holes, while the Be in the second group of materials adds only holes. Interest in these materials increased with the announcement of Curie temperatures as high as 110K [1, 2]. The ferromagnetic nature of these materials is believed to occur as the result of an RKKY-like interaction between Mn ions, which is moderated by the holes in the materials. As such, two ways to improve the T_c are to increase the amount of Mn participating in the ferromagnetic interaction (either by increasing the concentration of Mn or by increasing the likelihood of a given Mn's contribution to the interaction) or to increase the number of holes that moderate the interaction. Annealing the $Ga_{1-x}Mn_xAs$ and adding Be to it have been examined as a method to improve one of these possibilities.

Methods and Materials

X-ray absorption fine-structure (XAFS) spectroscopy is a technique that provides local structural information on the area around atoms of a specific element. This technique does not differentiate between atoms of the same element in different structural environments, so if the atoms of the element being studied are in more than one structural environment, the signals from each environment are combined. This method is well suited for examining these types of materials, since the Mn-edge energy is well separated from the energy of the edges of the other elements in the samples: Ga, As, and Be.

The samples were grown at Notre Dame in a Riber 32 R&D MBE system. The details of this growth can be found elsewhere [3, 4]. The $Ga_{1-x}Mn_xAs$ samples were grown with x = 0.08 and annealed to 280°C and 350°C. The crystal growers felt that one of the $Ga_{1-x}Mn_xAs$ samples was grown in such a way that the sample would be contaminated by MnAs because of the growth temperature. The $Ga_{1-x}Mn_xBe_yAs$ samples were grown with x = 0.05 and a range of values for y from 0.0 to 0.11. The Be-codoped samples are herein referred to by the Be cell temperature during growth rather than the percentage of Be grown. Table 1 shows the correlation between cell temperature and Be concentration.

TABLE 1. Correlation between Cell Temperature and Be Concentration.

Be Cell Temperature	Be Content, y
0	0
960	0.01
1038	0.03
1050	0.048
1060	0.08
1070	0.11

The experiments were conducted at MR-CAT beamline 10-ID at the APS. The first harmonic of the undulator was used with a 0.1-keV taper and an Si 111 monochromator to provide a beam at the energy of the Mn edge, 6.539 keV. A glass harmonic rejection mirror was used to remove higher-order harmonics from the beam so they would not contaminate the data. Because of the highly crystalline nature of the MBE-grown samples, Bragg reflection posed a threat to data collection. In order to remove this threat, the x-ray fluorescence was measured in grazing incidence geometry by using a 13-element solid-state detector. After data reduction was done by using standard methods, the data were fit by using the IFEFFIT program [5]. The theoretical scattering paths used to fit the data in IFEFFIT were generated by using FEFF 8.2 [6, 7].

Results

The chi data from the $Ga_{1-x}Mn_xAs$ were Fourier transformed from 2.4 to 12.5. The magnitude of this transform is shown in Fig. 1. The data show the similarities in the nearest-neighbor local structure around the Mn as a function of the annealing. The work in IFEFFIT showed that the as-grown sample and the optimally annealed samples are both best fit by a three-shell model of Mn substituting for Ga on the Ga site of a GaAs lattice (Mn_{Ga}). However, the other materials — overannealed and MnAs-contaminated — are not fit as

well by the Mn_{Ga} model. Other models, such as Mn interstitials surrounded by either Ga or As, metallic Mn, and MnAs, were also attempted; however, none of these models worked. Two-part combinations were then used to try to ascertain the percentage of Mn in different structural environments. This work still continues.

The $Ga_{1-x-y}Mn_xBe_yAs$ was also Fourier transformed from 2.4 to 12.5. The magnitude of this Fourier transform is shown in Fig. 2. The figure shows that the magnitude of the first-shell scattering decreases as the concentration of Be increases, which could be caused by a couple of things. This first possibility is simply an increase in the Debye-Waller factor, which is a measure of the disorder in the system. However, this possibility can be ruled out through examination of the χ data in Fig. 3, which show a decrease in the overallamplitude

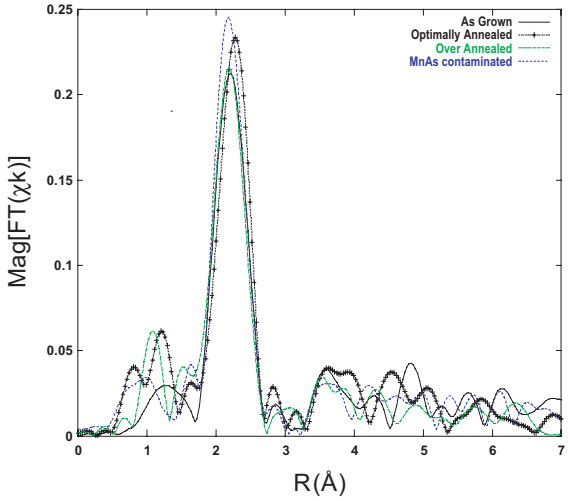

FIG. 1. Magnitude of Fourier Transform of $Ga_{1-x-y}Mn_xAs$.

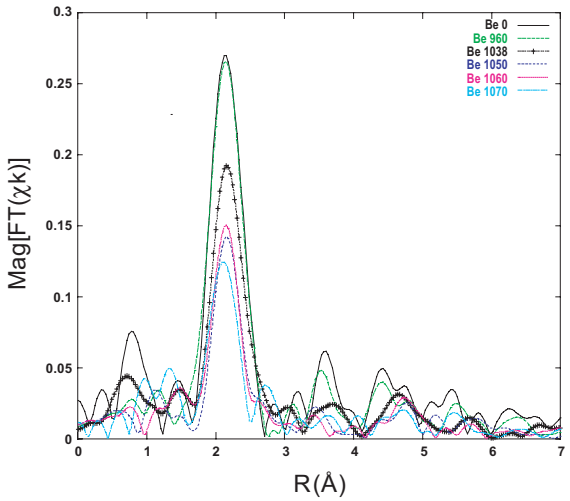

FIG. 2. Magnitude of Fourier Transform of $Ga_{1-x-y}Mn_xBe_yAs$.

of the χ function as the Be content increases. If the Debye-Waller factor caused the decrease in the magnitude of the first shell, then the expectation would be that the χ-data would match for the first several oscillations, then decrease at higher k values, and that the decrease possible would be more rapid for higher amounts of Be. The second possible cause of the change in amplitude is interference between the signals from different sites occupied by the Mn ions in the $Ga_{1-x-y}Mn_xBe_yAs$. Analysis following that train of thought has been pursued. Fitting by using up to three shells has led to the determination that Be 0 ($Ga_{0.95}Mn_{0.05}Be_0As$) is largely Mn_{Ga} (the substitutional model). The Be 960 ($Ga_{0.94}Mn_{0.05}Be_{0.01}As$) is also fit best by a three-shell model of Mn_{Ga}. However, the goodness of the fit when this model is used deteriorates very quickly beyond this amount of Be. The three-shell model Mn_{Ga} also fits the Be 1038 sample; however, the goodness of the fit is not as good as it was for the two previous samples. For the Be 1050, Be 1060, and Be 1070 samples, the three-shell Mn_{Ga} model does not fit the higher shells (second and third). Other models, such as tetragonal interstitial Mn ($Mn_{I\text{-}As}$ and $Mn_{I\text{-}Ga}$ surrounded by As and Ga, respectively), hexagonal interstitial Mn (Mn_{hex}), manganese arsenide (MnAs), and metallic Mn, also do not individually fit the data. Binary models, which used two of the aforementioned models while allowing the percentage of each model in the fit to vary, were attempted next. For the first two samples — Be 0 and Be 960 — the fitting always chose to use 100% of the Mn_{Ga} model. Examination of the Be 1038 sample showed that the binary models, which used approximately 89%, did not match the data as well as the Mn_{Ga} model. For the last three samples — Be 1050, Be 1060, and Be 1070 — the combination fits worked slightly better than the distorted Mn_{Ga} model.

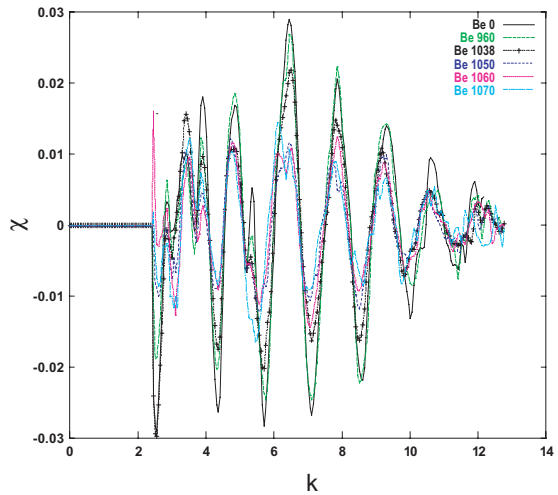

FIG. 3. Decrease in Overall Amplitude of χ Function as Be Increases.

However, the change in the χ^2 of the fit between the Mn_{Ga} model and the binary models was too small to be a statistical improvement.

Discussion

XAFS examinations of the Mn local structure in $Ga_{1-x}Mn_xAs$ and $Ga_{1-x-y}Mn_xBe_yAs$ materials have been conducted. The $Ga_{1-x}Mn_xAs$ materials, in which various annealing temperatures were examined, exhibited several structures that depended on the details of the annealing. The local structure of the Mn in as-grown material was found to be that of Mn in a substitutional environment. This was also found to be the case in the optimally annealed material, albeit with differing bond length changes and Debye-Waller factors. However, the overannealed material was not found to be primarily of this local structure, nor was it of a linear combination of the models investigated to this point.

The XAFS of the $Ga_{1-x-y}Mn_xBe_yAs$ materials was also found to be complicated. The samples with small amounts of Be — Be 0, Be 960, and Be 1038 — were found to be best modeled by the substitutional model three shells. The samples with higher levels of Be — Be 1050, Be 1060, and Be 1070 — were not as simple. The substitutional model did not provide a believable fit, nor did linear combinations of two models. The decrease in the magnitude of the Fourier transform of the first shell in this system, which has been shown to not be caused by an increase in the Debye-Waller factor, is still unexplained, but it could be caused by a combination of more than two local environments for the Mn. Multiple local structural environments for the Mn in the materials that were more heavily codoped with Be would not be extremely surprising; thus, the examination of such models continues.

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