Nature of magnetic coupling between Mn ions in as-grown Ga$_{1-x}$Mn$_x$As studied by x-ray magnetic circular dichroism

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The magnetic properties of as-grown Ga$_{1-x}$Mn$_x$As have been investigated by the systematic measurements of temperature and magnetic field dependent soft x-ray magnetic circular dichroism (XMCD). The intrinsic XMCD intensity at high temperatures obeys the Curie-Weiss law, but residual spin magnetic moment appears already around 100 K, significantly above Curie temperature ($T_C$), suggesting that short-range ferromagnetic correlations are developed above $T_C$. The present results also suggest that antiferromagnetic interaction between the substitutional and interstitial Mn ($Mn_{int}$) ions exists and that the amount of the $Mn_{int}$ affects $T_C$.

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Ga$_{1-x}$Mn$_x$As is a prototypical and most well-characterized diluted magnetic semiconductor (DMS) \cite{1}. Because Ga$_{1-x}$Mn$_x$As is grown under thermal non-equilibrium conditions, however, it is difficult to avoid the formation of various kinds of defects and/or disorder. In fact, Rutherford backscattering (RBS) channeling experiments for as-grown Ga$_{0.92}$Mn$_{0.08}$As samples has shown that as many as ~17 % of the total Mn ions may occupy the interstitial sites \cite{2}. It is therefore supposed that antiferromagnetic (AF) interaction between the substitutional Mn ($Mn_{sub}$) ions and interstitial Mn ($Mn_{int}$) ions may suppress the magnetic moment \cite{3,4}. In addition, the random substitution of Mn ions may create inhomogeneous Mn density distribution, which may lead to the development of ferromagnetic domains above Curie temperature ($T_C$) \cite{5}. The characterization of non-ferromagnetic Mn ions is therefore a clue to identify how they are related with the ferromagnetic ordering and eventually to improve the ferromagnetic properties of Ga$_{1-x}$Mn$_x$As samples. However, it has been difficult to extract the above information through conventional magnetization measurement due to the large diamagnetic response of the substrate and the unavoidable mixture of magnetic impurities.

X-ray magnetic circular dichroism (XMCD), which is an element specific magnetic probe, is a powerful technique to address the above issues. So far, several results of XMCD measurements on Ga$_{1-x}$Mn$_x$As have been reported \cite{6,7,8}. From $H$ dependent XMCD studies, the enhancement of XMCD intensity by post-annealing implies AF interaction between the $Mn_{sub}$ and $Mn_{int}$ ions \cite{8}. In the present study, in order to characterize the magnetic behaviors of the $Mn_{sub}$ and $Mn_{int}$, we have extended the approach and performed systematic temperature ($T$) and magnetic field ($H$) dependent XMCD studies in the Mn $L_{2,3}$ absorption edge region of Ga$_{1-x}$Mn$_x$As. We have found that short-range ferromagnetic correlations develop significantly above $T_C$ and that AF interaction between the $Mn_{sub}$ and $Mn_{int}$ is important to understand the magnetic properties of Ga$_{1-x}$Mn$_x$As.

We prepared two as-grown samples with different Mn concentrations; $x = 0.042$ and 0.078, whose $T_C$ was ~ 60 and 40 K, respectively, as determined by an Arrott plot of the anomalous Hall effect. To avoid surface oxidation, the sample had been covered immediately after the growth of Ga$_{1-x}$Mn$_x$As films by cap layers without exposure to air [As cap/GaAs cap (1nm)/Ga$_{1-x}$Mn$_x$As(20nm)/GaAs(001)]. The X-ray absorption spectroscopy (XAS) and XMCD measurements were performed at the helical undulator beam line BL23SU of SPring-8 \cite{9}. The XAS spectra were obtained by the total-electron yield mode. The measurements were done without a surface treatment and $H$ was applied to the sample perpendicular to the film surface.

Figures 1 (a) and 1 (b) show the XAS spectra ($\mu^+$ and $\mu^-$) in the photon energy region of the Mn $L_3$ absorption edge and the corresponding XMCD spectra, defined as $\mu^+ - \mu^-$, at $T = 20$ K and $H = -0.5$ T for $x = 0.042$ and 0.078. Here, $\mu^+$ ($\mu^-$) refers to the absorption coefficient for the photon helicity parallel (anti-parallel) to the Mn 3$d$ majority spin direction. The XAS spectra for both Mn concentrations have five structures labeled as $a$, $b$, $c$, $d$ and $e$. The average XAS spectra [defined by $(\mu^+ + \mu^-)/2$] have been normalized to 1 at structure $b$. The intensity ratio $c/b$ is very different between
FIG. 1: (Color online) Mn L3-edge XAS ($\mu^+$, $\mu^-$ and ($\mu^+$ + $\mu^-$)/2) and XMCD ($\mu^+$ - $\mu^-$) spectra of Ga$_{1-x}$Mn$_x$As taken at $T = 20$ K and $H = 0.5$ T for $x = 0.042$ (a) and $x = 0.078$ (b). Panels (c) and (d) show the $H$ dependence of the XMCD spectra for $x = 0.042$ and $x = 0.078$, respectively. Inset shows the difference XMCD spectra obtained by subtracting the XMCD spectra at $H = 0.5$ T.

$x = 0.042$ and 0.078, indicating that the spectra consist of two overlapping components. Figures 1 (c) and 1 (d) show the $H$ dependence of the XMCD spectra. As $H$ increases, XMCD structures corresponding to structures $c$, $d$ and $e$ are enhanced, particularly strongly for the $x = 0.042$ sample. One can see this behavior more clearly in the difference XMCD spectra obtained by subtracting the XMCD spectrum at 0.5 T from the spectra at $H = 1, 2, 4$ and 6 T as shown in the inset of Fig.1 (c) and (d). Recent XAS and XMCD studies have revealed that these structures ($c$, $d$, $e$) are ascribed to contamination of out-diffused Mn ions on the surface. The difference in the XAS intensity ratio $c/b$ is therefore naturally ascribed to the difference in the amount of Mn ions diffused into the cap layer or the surface region during the growth of GaAs on Ga$_{1-x}$Mn$_x$As. In the following, therefore, we shall neglect those extrinsic signals and focus only on intrinsic signals, particularly structure $b$, to investigate the intrinsic magnetic behavior.

In order to extract the intrinsic XAS spectrum, we assumed that structure $b$ could be ascribed to the intrinsic Mn ions as mentioned above. Therefore, we first obtained the extrinsic XAS spectrum as (XAS $x = 0.042$)−$p \times$ (XAS $x = 0.078$), where $p$ was chosen so that structure $b$ vanished. The intrinsic XAS spectrum was then obtained as (raw XAS)−$q \times$ (extrinsic XAS), where $q$ was determined so that the line shape of the intrinsic XAS spectrum agreed with that obtained from the fluorescence yield measurements. Next, in order to extract the intrinsic XMCD spectra, we first obtained the extrinsic XMCD spectrum as (XMCD at 6 T)−$a \times$ (XMCD at 0.5 T), where $a$ was chosen so that an XMCD structure corresponding to structure $b$ vanished by utilizing the fact that the ferromagnetic signals and hence the intrinsic signals should be dominant in the XMCD spectrum at low $H$. The intrinsic XMCD spectrum was then obtained as (XMCD at each $H$)−$\beta \times$ (extrinsic XMCD spectrum), where $\beta$ was chosen so that structure $c$ vanished. Figures 2 (a) and 2 (b) show the results of the decomposition of the XAS and XMCD spectra into the intrinsic and extrinsic components for $x = 0.042$ and 0.078, respectively. While the XMCD intensity is enhanced as $H$ increases and $T$ decreases, the line shapes of the intrinsic XMCD spectra are unchanged with $H$ and $T$. The line shapes of the intrinsic XAS and XMCD spectra for both Mn concentrations thus agree with each other as shown in Fig. 2 (c), indicating that the decomposition procedure was valid.

Using the intrinsic XAS and XMCD spectra, we have applied the XMCD sum rules, assuming the Mn 3d electron number $N_d = 5.1$, and estimated the spin magnetic moment ($M_S$) at $T = 20$ K and $H = 0.5$ T to be $M_S = 2.5 \pm 0.2$ and 1.7±0.2 ($\mu_B$ per Mn) for $x = 0.042$ and 0.078, respectively. These $M_S$ values are much larger than those obtained in the early studies on oxidized surfaces and comparable to the recent ones on etched surfaces, indicating that the cap layer protected the ferromagnetic properties of Ga$_{1-x}$Mn$_x$As. The ratio $M_L/M_S$ is estimated to be 0.07 for both concentrations, where $M_L$ is the value of the orbital magnetic moment, showing that the intrinsic Mn ion has a finite, although small, $M_L$, probably because of certain deviation from the pure Mn$^{2+}$ (d$^5$) state.

The $T$ dependence of $M_S$ from the XMCD signal for $H = 6$ T is plotted in Fig. 3 (a). As $T$ decreases, the XMCD signal is increased monotonously except for the discontinuity at around $T_C$ ($\sim 60$ K for $x = 0.042$, $\sim 40$ K for $x = 0.078$). This discontinuity probably reflects the ferromagnetic ordering which aligns the magnetization parallel to the sample surface, the easy axis of magnetization in the films. It should be noted that $M_S$ increases monotonously even well below $T_C$ as $T$ decreases, indicating that full spin polarization is not achieved even well below $T_C$. For $x = 0.078$, the $T$ dependence for $H =$
1 T shows essentially the same behavior as that for 6 T. Figure 3 (b) shows the inverse of $M_S$ plotted in Fig 3 (a). The high-temperature part is well described by the Curie-Weiss (CW) law, independent of $H$ as shown in the inset of Fig. 3 (b).

Figure 4 shows the $H$ dependence of $M_S$ at several temperatures for $x = 0.042$ [panel (a)] and 0.078 [panel (b)]. $M_S$ of the intrinsic component is increased rapidly from $H = 0.1$ to 0.5 T, due to the re-orientation of the ferromagnetic moment from the in-plane to out-of-plane directions. Above 0.5 T, $M_S$ is increased almost linearly as a function of $H$. We have plotted the $T$ dependence of $M_S|_{H→0T}$ obtained from the linear extrapolation of $M_S$ at high fields to $H = 0$ T and $\partial M_S/\partial H|_{H>0.5T}$ (µB/T per Mn) (the susceptibility of the paramagnetic component) in Fig. 4 (c) and (d), respectively. For the extrinsic component, $M_S|_{H→0T}$ is vanishingly small at all temperatures and $\partial M_S/\partial H|_{H>0.5T}$ is increased as $T$ decreases following the CW law, indicating that the extrinsic component is paramagnetic and decoupled from the ferromagnetism of the intrinsic component. As for the ferromagnetic component, $M_S|_{H→0T}$ [Fig. 4 (c)] is correlated with the deviation from the CW law below $\sim 100$ K [Fig. 3 (b)]. Well below $T_C$, $M_S|_{H→0T}$ still continues to increase with decreasing $T$, indicating the inhomogeneous nature of the ferromagnetism. As for $\partial M_S/\partial H|_{H>0.5T}$, unlike the extrinsic component, it saturates around $T_C$ and is not increased as $T$ further decreases. The appearance and increase of $M_S|_{H→0T}$ between $T_C$ and $\sim 100$ K [Fig. 4 (c)] strongly suggest that short-range ferromagnetic correlations start to develop and ferromagnetic domains form before the long-range order is established at macroscopic $T_C$. Each ferromagnetic domain may have different ferromagnetic behavior due to the spatial distribution of $T_C$ in the as-grown samples. Those results may correspond to the theoretical prediction that ferromagnetic domains develop above $T_C$ when there is magnetic inhomogeneity.

The suppression of the CW-like increase of $\partial M_S/\partial H|_{H>0.5T}$ below $T_C$ in both samples indicates that AF interaction between the ferromagnetic Mn i.e., Mn$_{sub}$ and non-ferromagnetic (or paramagnetic) Mn such as Mn$_{int}$. The recent $H$ dependent XMCD study of Ga$_{1-x}$Mn$_x$As shows that $\partial M_S/\partial H|_{H>0.5T}$ becomes small and $M_S|_{H→0T}$ becomes large after post-annealing, suggesting that the changes are caused by a reduction of Mn$_{int}$. In the present study, $\partial M_S/\partial H|_{H>0.5T}$ and $M_S|_{H→0T}$ are smaller for $x = 0.078$ than for $x = 0.042$ [Fig. 4 (c) and (d)], suggesting that AF interaction becomes stronger for $x = 0.078$ than that for $x = 0.042$. This is reasonable because the number of Mn$_{int}$ is expected to be larger for larger Mn concentration. Assuming that $M_S$ per the Mn$_{sub}$ is 5 (µB per Mn) and $M_S$ of the Mn$_{int}$ is antiparallel to that of Mn$_{sub}$, the ratio of Mn$_{int}$ atoms in the intrinsic component ($R_{int}$) is estimated as 0.26 for $x = 0.042$ and 0.33 for $x = 0.078$ from $M_S|_{H→0T}$ at 20 K. This is consistent with the result of the RBS experiment, which $R_{int}$ is estimated as 0.17 for an as-grown sample with $T_C = 67$ K, indicating that $T_C$ is strongly correlated with the amount of Mn$_{int}$. We have fitted the susceptibility $\partial M_S/\partial H|_{H=0T}$ (µB/T per Mn) of the intrinsic component above 100 K [Fig. 3 (b)] to the CW law with an offset, $\partial M_S/\partial H|_{H=0T} = N_x C/(T - \Theta) + \partial M_S/\partial H|_0$, where $C = (g\mu_B)^2S(S+1)/3k_B$ is the Curie constant, $\Theta$ is the Weiss temperature, $\partial M_S/\partial H|_0$ is the constant offset, $N_x$ is the number of magnetic Mn ions in the sample with Mn concentration $x$, and $g$ is the $g$ factor. $\Theta$ is estimated to be 68±5 K for $x = 0.042$ and 69±3 K for $x = 0.078$. $\partial M_S/\partial H|_0$ is estimated to be of order of
\(10^{-3}\) for both samples. Assuming \(g = 2, S = 5/2\) and \(\Theta = 68\) K, one obtains \(N_{0.042} = 0.97\) and \(N_{0.078} = 0.67\). This result strongly suggests that most of the intrinsic Mn ions in the \(x = 0.042\) sample participate in the paramagnetism above \(\sim 100\) K and the paramagnetism in the \(x = 0.078\) sample is suppressed even at high temperatures, again implying that the AF interaction is stronger and more influential in the \(x = 0.078\) sample.

In conclusion, we have investigated the \(T, H\) and Mn concentration dependences of the ferromagnetism in as-grown \(\text{Ga}_{1-x}\text{Mn}_x\text{As}\) samples by XMCD measurements to extract the intrinsic magnetic component. The XMCD intensity deviates from the CW law below \(\sim 100\) K, indicating that the ferromagnetic moment starts to form at \(\sim 100\) K and that the short-range ferromagnetic correlations develop significantly above \(T_C\). The high-field magnetic susceptibility becomes \(T\)-independent below \(T_C\), indicating that the AF interaction between the Mn_{sub} and Mn_{int} ions, which becomes strong as the Mn concentration \(x\) increases, plays an important role to determine the magnetic behavior of \(\text{Ga}_{1-x}\text{Mn}_x\text{As}\). In addition, the amount of the Mn_{int} ions should be strongly related with \(T_C\). The present experimental findings should give valuable insight into the inhomogeneous magnetic properties of many DMS’s. In future studies, it is very important to perform a detail \(T\) and \(H\) dependent XMCD study for a post-annealed samples.

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