Nature of Magnetic Coupling between Mn Ions in As-Grown $Ga_{1-x}Mn_xAs$ Studied by X-Ray Magnetic Circular Dichroism

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The magnetic properties of as-grown $Ga_{1-x}Mn_xAs$ 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 a residual spin magnetic moment appears already around 100 K, significantly above the Curie temperature (T_C), suggesting that short-range ferromagnetic correlations are developed above T_C. The present results also suggest that the 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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$Ga_{1-x}Mn_xAs$ is a prototypical and most well-characterized diluted magnetic semiconductor (DMS) [1]. Because $Ga_{1-x}Mn_xAs$ is grown under thermal nonequilibrium conditions, however, it is difficult to avoid the formation of various kinds of defects and/or disorders. In fact, Rutherford backscattering (RBS) channeling experiments for as-grown $Ga_{0.92}Mn_{0.08}As$ samples have shown that as many as ~17% of the total Mn ions may occupy the interstitial sites [2]. It is therefore supposed that the antiferromagnetic (AF) interaction between the substitutional Mn (Mn_{sub}) ions and interstitial Mn (Mn_{int}) ions may suppress the magnetic moment [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) [5]. The characterization of nonferromagnetic Mn ions is therefore a clue to identify how they are related with the ferromagnetic ordering and eventually to improve the ferromagnetic properties of $Ga_{1-x}Mn_xAs$ 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 $Ga_{1-x}Mn_xAs$ have been reported [6–8]. From magnetic field (H) dependent XMCD studies, the enhancement of XMCD intensity by post-annealing implies AF interaction between the Mn_{sub} and Mn_{int} ions has been proposed [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 H dependent XMCD studies in the Mn $L_{2,3}$ absorption edge region of $Ga_{1-x}Mn_xAs$. The systematic dependences of XMCD signals help us to obtain important information about details of magnetic properties, namely, characteristic behaviors of the ferromagnetic and paramagnetic components of a specific magnetic element and even magnetic interaction between them, on a microscopic level [9,10]. We have also 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 $Ga_{1-x}Mn_xAs$.

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 $Ga_{1-x}Mn_xAs$ films by cap layers without exposure to air [As cap/GaAs cap(1 nm)/$Ga_{1-x}Mn_xAs$(20 nm)/GaAs(001)]. The x-ray absorption spectroscopy (XAS) and XMCD measurements were performed at the helical undulator beam line BL23SU of SPring-8 [11,12]. 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 (μ^+ and μ^-) 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, μ^+ (μ^-) refers to the absorption coeffi-

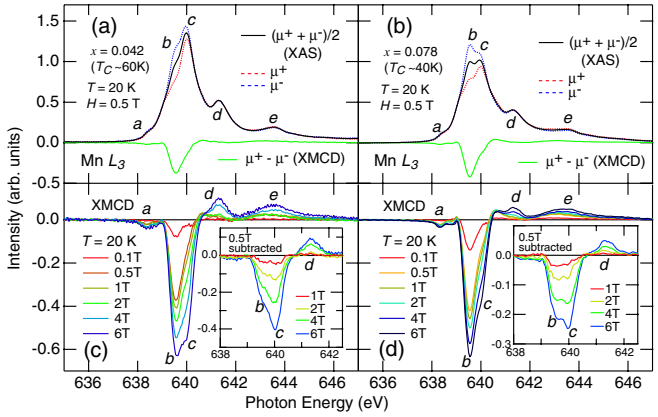

FIG. 1 (color online). Mn L_3-edge XAS [μ^+, μ^- and $(\mu^+ + \mu^-)/2$] and XMCD ($\mu^+ - \mu^-$) spectra of $Ga_{1-x}Mn_xAs$ taken at $T = 20$ K and $H = 0.5$ T for $x = 0.042$ (a) and $x = 0.078$ (b). Panels (c) and (d) show the H dependence of the XMCD spectra for $x = 0.042$ and $x = 0.078$, respectively. Inset shows the difference XMCD spectra obtained by subtracting the XMCD spectrum at $H = 0.5$ T.

cient for the photon helicity parallel (antiparallel) to the Mn $3d$ 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 $x = 0.042$ 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 Figs. 1(c) and 1(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 [7,13,14]. 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 $Ga_{1-x}Mn_xAs$. 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(XAS $x = 0.078$), where p was chosen so that structure b vanished. The *intrinsic* XAS spectrum was then obtained as (raw XAS) $-$ q(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 [13,14]. Next, in order to extract the *intrinsic* XMCD spectra, we first obtained the *extrinsic* XMCD spectrum as (XMCD at 6 T) $-$ α(XMCD at 0.5 T), where α 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) $-$ β(extrinsic XMCD spectrum), where β 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 [15,16], assuming the Mn $3d$ electron number $N_d = 5.1$ [8], 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 (μ_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 [6] and comparable to the recent ones on etched surfaces [8], indicating that the cap layer protected the ferromagnetic properties of $Ga_{1-x}Mn_xAs$. 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 increases monotonically 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 ferromag-

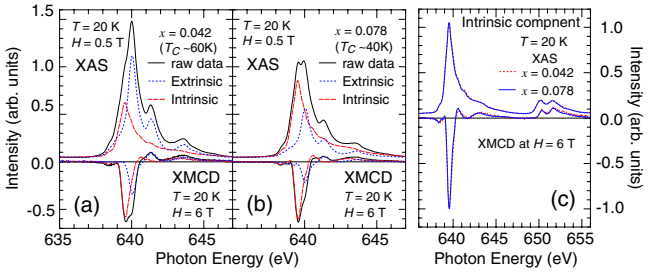

FIG. 2 (color online). Decomposition of the XAS and XMCD spectra of $Ga_{1-x}Mn_xAs$ into the intrinsic and extrinsic components for $x = 0.042$ (a) and for $x = 0.078$ (b) in the Mn L_3 edge region. Panel (c) shows comparison of the line shapes of the *intrinsic* XAS and XMCD spectra between $x = 0.042$ and 0.078, normalized to the peak heights.

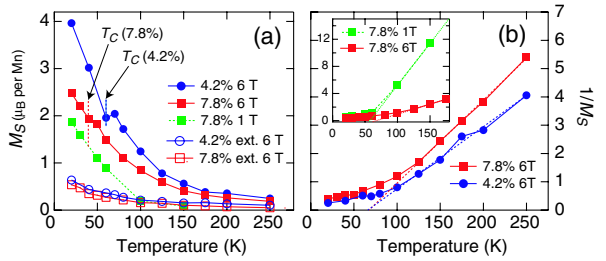

FIG. 3 (color online). T dependence of the spin magnetic moment M_S. (a) T dependence of M_S for $H = 6$ T. For $x = 0.078$, results for $H = 1$ T are also plotted. Open symbols show that of the extrinsic component at $H = 6$ T. (b) T dependence of the inverse of M_S. Inset shows comparison between 1 and 6 T for $x = 0.078$.

netic ordering which aligns the magnetization parallel to the sample surface, the easy axis of magnetization in the films [17]. It should be noted that M_S increases monotonically 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 at $T = 20$ K, due to the reorientation of the ferromagnetic moment from the in-plane to out-of-plane directions [17]. Above 0.5 T, M_S is increased almost linearly as a function of H. We have plotted the T dependence of $M_S|_{H\to 0\ \mathrm{T}}$ obtained from the linear extrapolation of M_S at high fields to $H = 0$ T and

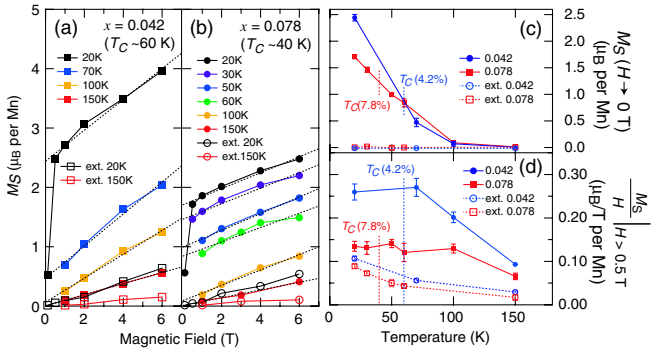

FIG. 4 (color online). H dependence of M_S for $x = 0.042$ (a) and for $x = 0.078$ (b) at several temperatures. Dashed lines show fitted straight lines above 0.5 T. (c) T dependence of the residual magnetization $M_S|_{H\to 0\ \mathrm{T}}$ (M_S for $H \to 0$ T). Open symbols show that of the extrinsic component. (d) T dependence of the slope of the M_S-H curve above 0.5 T, i.e., the high-field magnetic susceptibility ($\partial M_S/\partial H|_{H>0.5\ \mathrm{T}}$). Open symbols show that of the extrinsic component.

$\partial M_S/\partial H|_{H>0.5\ \mathrm{T}}$ (μ_B/T per Mn) (the susceptibility of the paramagnetic component) in Figs. 4(c) and 4(d), respectively. For the extrinsic component, $M_S|_{H\to 0\ \mathrm{T}}$ is vanishingly small at all temperatures and $\partial M_S/\partial H|_{H>0.5\ \mathrm{T}}$ 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, $M_S|_{H\to 0\ \mathrm{T}}$ is steeply increased below ~100 K, i.e., from somewhat above T_C. The T dependence of $M_S|_{H\to 0\ \mathrm{T}}$ [Fig. 4(c)] is correlated with the deviation from the CW law below ~100 K [Fig. 3(b)]. Well below T_C, $M_S|_{H\to 0\ \mathrm{T}}$ still continues to increase with decreasing T, indicating the inhomogeneous nature of the ferromagnetism. As for $\partial M_S/\partial H|_{H>0.5\ \mathrm{T}}$, unlike the extrinsic component, it saturates around T_C and is not increased as T further decreases. The appearance and increase of $M_S|_{H\to 0\ \mathrm{T}}$ between T_C and ~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 [5].

The suppression of the CW-like increase of $\partial M_S/\partial H|_{H>0.5\ \mathrm{T}}$ below T_C in both samples indicates AF interaction between the ferromagnetic Mn, i.e., $\mathrm{Mn_{sub}}$ and nonferromagnetic (or paramagnetic) Mn such as $\mathrm{Mn_{int}}$. The recent H dependent XMCD study of $\mathrm{Ga_{1-x}Mn_xAs}$ shows that $\partial M_S/\partial H|_{H>0.5\ \mathrm{T}}$ becomes small and $M_S|_{H\to 0\ \mathrm{T}}$ becomes large after post-annealing, suggesting that the changes are caused by a reduction of $\mathrm{Mn_{int}}$ [8]. In the present study, $\partial M_S/\partial H|_{H>0.5\ \mathrm{T}}$ and $M_S|_{H\to 0\ \mathrm{T}}$ are smaller for $x = 0.078$ than for $x = 0.042$ [Figs. 4(c) and 4(d)], suggesting that AF interaction becomes stronger for $x = 0.078$ than that for $x = 0.042$. This is reasonable because the number of $\mathrm{Mn_{int}}$ is expected to be larger for larger Mn concentration. Assuming that M_S per the $\mathrm{Mn_{sub}}$ is 5 (μ_B per Mn) and M_S of the $\mathrm{Mn_{int}}$ is antiparallel to that of $\mathrm{Mn_{sub}}$, the ratio of $\mathrm{Mn_{int}}$ ions in the intrinsic component (R_{int}) is estimated as 0.26 for $x = 0.042$ and 0.33 for $x = 0.078$ from $M_S|_{H\to 0\ \mathrm{T}}$ at $T = 20$ K. This is consistent with the result of the RBS experiment [2], 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 $\mathrm{Mn_{int}}$. We have fitted the susceptibility $\partial M_S/\partial H|_{H=6\ \mathrm{T}}$ (μ_B/T per Mn) of the intrinsic component above 100 K [Fig. 3(b)] to the CW law with an offset, $\partial M_S/\partial H|_{H=6\ \mathrm{T}} = N_x C/(T - \Theta) + \partial M_S/\partial H|_0$, where $C = (g\mu_B)^2 S(S+1)/3k_B$ is the Curie constant, Θ 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. Θ 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 the order of $\sim 10^{-3}$ 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 ~ 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 $Ga_{1-x}Mn_xAs$ samples by XMCD measurements to extract the intrinsic magnetic component. The XMCD intensity deviates from the CW law below ~ 100 K, indicating that the ferromagnetic moment starts to form at ~ 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 $Ga_{1-x}Mn_xAs$. 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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