Chemical and Magnetic profile of magnetic semiconductors as probed by Polarized Neutron Reflectivity

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Abstract

We investigate the depth dependency of magnetic species in co-doped dilute magnetic semiconductor (DMS) specimens. We also compare the reliability in nuclear and magnetization depth profile of these specimens at different polarized neutron reflectivity (PNR) instruments. These reflectometers were not only angle dispersive but also wavelength dispersive instrument. Measurements, indicate a segregation of DMS species on to the top into the cap-layer for lower Fe-doping. However, for higher Fe-doping, as we alter the doping concentrations of magnetic species, it indicates no segregation and lower clustering tendencies. Thus sensitive depth-profiling, for specimens with such low magnetic-ion concentrations, may not be a challenge for brighter sources and careful measurements. Our results shows that the homogeneity can be achieved with Fe co-doping within the Ge matrix which can make it a potential candidate for spintronic applications.

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I. INTRODUCTION

A. Ge based Magnetic semiconductors

In recent years one of the remarkable achievements in spintronics was the observation of hole-mediated ferromagnetism in III-V compounds.¹ However, the growth of group-IV ferromagnetic (FM) semiconductors such as $\text{Mn}_x\text{Ge}_{1-x}$ has also triggered strong interest in searching for higher ordering temperatures T_C in Ge-based compounds.² Trivalent state of the Mn ion, Mn^{3+} (d4, $S = 2$) is usually coexistent with divalent Mn^{2+} (d5, $S = 5/2$). However, Mn^{2+} is necessary for high-temperature ferromagnetism and can be enhanced by appropriate co-doping which are substituted for Ge. These ions, acting as acceptors, generate holes (p-type carriers) that mediate the ferromagnetic exchange interaction. Introducing additional electrons (n-type carriers), on the other hand, can fill the empty Mn d states in the gap, destroying the ferromagnetism.

An ideal magnetic substitution would have increased the magnetization and hence the T_C . Low temperature post-growth annealing has been shown to significantly affect the T_C as diffusion of Mn into the layer may redistribute the as-grown Mn site occupation, initialized during molecular beam epitaxial (MBE) growth. However, Mn atoms are often susceptible to surface segregation or form segregated phases³ during annealing. Such phases make the interpretation of ferromagnetic behavior ambiguous as isolated domains may be formed.

Recently, it was reported^{4,5} on the synthesis of another candidate for a DMS compound: an alloy of Ge, Fe, and Mn. The addition of Fe to MnGe enables us to conserve the epitaxial growth for higher total concentrations of magnetic species, which results in an increase of T_C . The alloy films are prepared by growing repeatedly Ge/Mn/Fe trilayers with various thicknesses of the Ge base layers. When the Ge thickness becomes comparable with the diffusion length of Mn and Fe in Ge, a homogeneous material without interfaces is formed as confirmed by X-ray reflectivity (XRR).

Transition metals are susceptible to form heterogeneous regions within Ge matrix due to their low solubility which may not be completely avoidable even with the help of co-doping process. Thus it is important to know the depth dependent segregation of magnetic species also within such co-doped DMS specimens. Such a study can be extremely sensitive to the quality of the data measured and its subsequent analysis. Thus we present here a detailed

investigation that identifies and distinguish such magnetic segregation or non-segregation within the same semiconductor matrix.

This paper is organized as follows: Firstly, we describe the interest in our DMS specimens in particular as they are co-doped with Fe and Mn in alternate concentrations. Secondly, we describe the main experimental technique which is polarized neutron reflectivity. Thirdly, it is followed by comparing the instruments at which the measurements are performed. Fourthly, we discuss upon two different models that we employ in analysing the data. Finally we present a comparative study of the polarized neutron reflectivity data obtained from various instruments on different neutron sources, with the purpose to understand the depth dependent segregation of magnetic species in co-doped DMS specimens.

B. Co-doping with alternating composition of magnetic species

Here, we consider two samples with different compositions: $[\text{Ge}(40 \text{ \AA})/\text{Fe}(4 \text{ \AA})/\text{Mn}(2 \text{ \AA})]_{\times 11}/\text{ZnS}(500 \text{ \AA})$ named DMS4Fe2Mn and $[\text{Ge}(40 \text{ \AA})/\text{Fe}(2 \text{ \AA})/\text{Mn}(4 \text{ \AA})]_{\times 11}/\text{ZnS}(500 \text{ \AA})$ named DMS2Fe4Mn.

These samples are particularly interesting as they are covered with thick cap-layers and therefore become a challenge in the extraction for the depth profile, not possible by other techniques. More particularly when they lack in periodic layer structures and thus evaluating the Fourier transformed spectra is even more susceptible to complication.

The samples are grown by MBE, the details of which have been given elsewhere.⁵ For an annealing temperature $T_A = 300^\circ\text{C}$ a homogeneous alloy is observed by XRR measurements.⁶ Magnetization measurements by a superconducting quantum interference device (SQUID) and magnetotransport measurements reveal ferromagnetic ordering, but show two different T_C s at 205 K and above 300 K for "DMS2Fe4Mn", which we relate to two magnetic phases. Interestingly, "DMS4Fe2Mn" does not show the high- T_C phase and appears in the transmission electron microscope (TEM) picture to be fairly homogeneous compared to the other samples.^{5,6} TEM indeed showed the formation of precipitates depending upon the content of magnetic species⁵ for the two compositions. A 50 nm of cap-layer (ZnS) on top imposes a serious limitation in extracting the changes in non-magnetic SLD profiles by x-ray after the samples are annealed⁶.

The role of chemical composition, magnetic composition and its diffusion in DMS com-

pounds can be explored by a depth sensitive technique such as polarized neutron reflectivity (PNR).^{7,8} Such information would be a help in growing uniform films with higher T_C . However, from the earlier measurements of the specimens on the HADAS reflectometer at FRJ-2,⁶ depth-dependent profile of buried magnetic species was found to be largely restricted by the low signal-to-background ratio. Here, we report on the PNR investigation of any variation in the Mn-Fe distribution with depth after annealing for the homogeneous (DMS4Fe2Mn) and inhomogeneous (DMS2Fe4Mn) specimens.

For the identification of magnetization in various spintronic materials such as interlayer-coupled systems or exchange bias systems⁹ or in magnetic semiconducting systems⁷, depth sensitive neutron scattering under grazing incidence¹⁰ with polarization analysis has been proven decisive. Due to the interaction between polarized neutrons and magnetic moments in the specimen, polarized neutron reflectivity (PNR) is sensitive to the in-plane magnetization for a homogeneous film on a *microscopic* scale and helps in vector-magnetometry of buried interfaces.

II. EXPERIMENT

Over the years, there has been a constant urge to develop new reflectometers on brighter sources. Different reflectometers often use different polarization technique and different options for neutron optical components such as flippers and polrizer/analyzer. In fact it is often felt that it would be quite useful to present the data from different PNR instruments (measuring the same specimens), including angle dispersive and wavelength dispersive instrument, with respect to their reliability of obtaining a proper nuclear and magnetization depth profile. This has not been done yet.

We take this opportunity to use our specimens in measuring at different reflectometers with the aim of digging out the magnetic and compositional depth profile while exploiting the various extrinsic parameters involved with a reflectometer. Our specimens serve an unique example of magnetic-multilayered structure with low magnetic concentration as we show the respective quantitative data analysis in deducing comparative magnetization profiles. Depth profiling of magnetic semiconductors are particularly challenging as they have very small concentration of magnetic species doped in, as compared to any other. This paper, however, does not intend to state the superiority or inferiority of one reflectometer over the

others, but simply tries to convey the practical factors that are to be taken care of or to be incorporated, while measuring such specimens.

A. Reflectometers

Reflectometers have been constructed at both steady state and pulsed neutron sources. The reflectivity is solely a function of the momentum transfer along the z direction, Q_z : a range of Q_z can be spanned either by changing the wavelength, and keeping fixed the angle of incidence, or by changing the angle of incidence at fixed wavelength. In the former mode the wavelength is selected by Bragg-reflecting the beam from the moderator with a crystal monochromator. In the second mode the neutron beam is chopped in short pulses: the neutron wavelength is sorted out by the time-of-flight (TOF) from chopper to detector. Reflectometers built at steady-state sources are of both kind, while at pulsed sources only TOF reflectometers are feasible. Both types of instruments have distinct advantages. In a TOF instrument a substantial region of Q_z is covered simultaneously, without changing the footprint on the sample, by the entire neutron spectrum. On the other hand, with a monochromator instrument one can use all available neutrons to measure the intensities at a selected value of Q_z .

We performed measurements of the specimens on various neutron reflectometers, pulsed (TOF) and steady-state sources. The instruments are TREFF(HADAS) at FMR-2(FRJ-2).^{6,11} (Forshunreactor Juelich, Germany)⁶, D17 at the ILL (Institut Laue-Langevin, France)¹² and CRISP at ISIS (United Kingdom)¹³. Each of these instruments has some unique features distinctly different from the other (discussed later). This makes the data obtained from each of them interesting to look into with respect to the effect of such changes.

On HADAS, and D17, polarization channels of the specular reflectivities are measured by 2-dimensional position sensitive detector, whereas on CRISP ^3He single detector was used. The measurements are done at different external fields H_a , in monochromatic mode for wavelength $\lambda=5.5\text{\AA}$ on D17 ($\lambda=4.5\text{\AA}$ on HADAS and $\lambda=4.73\text{\AA}$ on TREFF) and TOF mode for two different incident angles (0.25° and 0.5°) on CRISP covering the normal wave vector transfer ($Q_\perp = \frac{2\pi}{\lambda}[\sin(\alpha_i)+\sin(\alpha_f)]$) ranging from 0.005 to $0.1\text{\AA}^{-1}$. The measurements from CRISP are done without polarization analysis. In specular geometry the angle of incidence α_i equals the final angle α_f , and λ from a band is selected by the monochromator

(HADAS/TREFF and D17) or by set of chopper selecting the wavelength band for the pulsed source (CRISP). All measurements are done after the sample was cooled to 50 K and 250 K from RT by a cryomagnet on D17 and a continuous flow cryostat (inserted between an electromagnet) on HADAS, TREFF and CRISP.

B. Polarized neutron scattering

PNR is sensitive to the nuclear and in-plane magnetic composition throughout the depth of the sample (the neutron absorption cross-sections for the atomic species in the sample are negligible). The scattering-length densities of the magnetic specimen is given by either the sum or difference of the nuclear (ρ_n) and magnetic (ρ_m) components. The neutron interaction potential is given by:

$$\hat{V} = \frac{2\pi\hbar^2}{m} N b_n + \mu_N \hat{\vec{\sigma}} \cdot \vec{B} \quad (1)$$

$$V \propto (\rho_n \pm \rho_m),$$

where N is the atomic density, b_n the coherent nuclear scattering length, m the neutron mass, B the internal magnetic field of the specimen, and $\vec{\sigma}$ represents the operator associated with the Pauli spin matrices while μ_N being the nuclear magneton. The scattering-length densities (SLD) of a magnetic specimen are given by either the sum or difference of the nuclear (ρ_n) and magnetic (ρ_m) components. The $\pm$ signs refers to the spin-up and spin-down states of the incident neutron with respect to the polarization of the specimen.

The reflectivity is calculated by applying the time-independent Schrödinger equation for the neutron wavefunction inside and outside the specimen. One can solve the equation by taking into account the spin dependencies of the scattering potential and the neutron wave function. In this way we get the expressions for non spin-flip (NSF) and spin-flip (SF) scattering. The NSF scattering amplitude provides information about $\rho_n \pm \rho_m \cos\phi_A$, *i.e.* the magnetization component $M_{\parallel}$ parallel or anti-parallel to the applied field, where ϕ_A is the angle between the magnetization direction $\vec{M}$ and the applied field $\vec{H}_a$. The SF channels measure $\rho_m^2 \sin^2\phi_A$, *i.e.* the magnetization component $M_{\perp}$ perpendicular to the applied field. In this approach, the magnetic scattering length b_m ($\rho_m = N b_m$) includes the magnetization M and the neutron magnetic moment μ_N .

Earlier,⁷ a quantitative information on depth profile has been shown for GaMnAs type of specimens. Exact reflection coefficients can be retrieved by the dynamical approach (low Q) within the Parratt formalism.¹⁰ Here a model density profile is considered (prior knowledge of the scattering density) which should be sufficiently close to the correct one. We fit our data within the dynamical approach.

The quality of the fits are found to be similar to that of Kirby *et al.*⁷ which also rely on a similar dynamical range as that of ours. Regarding the sensitivity of our measurements as compared to that of Kirby *et al.*,⁷ one may recall that our total thickness of DMS is lower. But this may have been largely compensated by a much higher concentration of magnetic species per unit thickness. On the other hand, similar thicknesses of the cap-layer and that of the DMS (≈ 500 Å) may have reduced the effective sensitivity.

III. RESULTS

Figure 1 shows the measurements for both specimens, at 50 K and at saturating applied fields. The specular reflectivities in the non-spin-flip (NSF) channels (R_{++} and R_{--}) are shown for the HADAS measurements. Here + and - sign refers to the intensity R represent the polarization parallel and antiparallel to the guiding field. The SF reflectivities (R_{+-} and R_{-+}) are always found to remain below the background intensities (comparing them with that in saturation) and are due to the inefficiencies of the polarizer or analyzer components. As we do not observe any significant SF scattering in HADAS⁶, we do not opt to measure/show the SF scattering in CRISP/D17/TREFF data. The background level was included in all fits as well as the polarization efficiencies were taken care of in the fitting routine. The TREFF data show a comparatively similar background as that of CRISP.

A splitting of the NSF reflectivity channels can be observed for both the specimens at an applied field corresponding to the saturation field (e.g. at $H_a = 2000$ Oe). The splitting is due to the difference in the index of refraction of spin up and spin down neutrons travelling in a magnetic medium. The splitting at low Q ($\sim 0.015 \text{ \AA}^{-1}$) indicates the presence of a ferromagnetic moment pointing along H_a . It is visible only at 50 K for both specimens. Similar contrast is seen for "DMS2Fe4Mn" even at somewhat lower fields at 50 K, and this net magnetization was seen pronounced at higher fields even at 250 K.

Figure 2 compares the spin-asymmetry (SA) (difference in R_{++} and R_{--} divided by the

sum of the two) at 50 K and at saturation. The spin asymmetry determines the averaged magnetic moment of the film and the peak amplitudes are largely determined by the magnitude of the net magnetization within the film. Oscillations in SA (recast of the measured data) are observed in the CRISP data, however, they suffer from large error bars specially at higher Q-range. On the other hand, even if the error bars are comparatively lower, the signal is seen to smear out in the background for the HADAS as well as for the D17 data at higher Q-range. The data from TREFF also retains the oscillations for similar Q-range.

IV. DISCUSSION

A. Comparison of the data from various reflectometers

As the measurements are from the same two samples under similar conditions but on three (four) reflectometers, we compare the respective measurement parameters to account for their differences in the spectrum.

One may recall that

$$\Delta Q/Q = \sqrt{\cot^2 \alpha_i (\Delta \alpha_i)^2 + \left(\frac{\Delta \lambda}{\lambda}\right)^2}, \quad (2)$$

which can be expressed as (for small α_i , $\cos \alpha_i \sim 1$ and $\sin \alpha_i \sim \alpha_i$)

$$\Delta Q/Q = \sqrt{\left(\frac{\Delta \alpha_i}{\alpha_i}\right)^2 + \left(\frac{\Delta \lambda}{\lambda}\right)^2} \quad (3)$$

The wavelength resolution and the angular resolution are determined by $\frac{\Delta \lambda}{\lambda}$ and $\frac{\Delta \alpha_i}{\alpha_i}$ respectively, as the wavelength

$$\lambda = \frac{4\pi \sin \alpha_i}{Q} \quad (4)$$

(Q=momentum transfer vector). Here $\Delta \lambda$ and $\Delta \alpha_i$ are the uncertainties in wavelength and angle respectively. The wavelength resolution was fixed (by the neutron monochromator) for D17 (optionally chosen in the present case), TREFF and HADAS. For CRISP this can be made variable with choppers. The angular resolution, on the other hand, can be adjusted by using a pair of slits in front of the sample (and also on the binning of the data on the detector).

HADAS/TREFF measurements were done with a wavelength resolution ($\Delta \lambda/\lambda$) of 1.5% while at D17 and CRISP it was around 4% and 3% respectively. The difference between TREFF and HADAS being primarily the neutron flux from the high-flux reactor FRM-2 in

Munich as compared to that from FRJ-2 in Juelich, as the instrument was recommissioned. This gives a direct example on the effect of flux on the data. A further comparison can be made following the HADAS and TREFF data as the angular resolution was restricted for TREFF (with same wavelength resolution) as compared to that for HADAS. The relaxed angular resolution (which in turn relaxes the overall Q resolution) and low neutron flux with with formidable background was found not to be suitable for very sensitive data analysis.

D17 being based on a high-flux reactor, the measurements were done with relaxed resolution. A similar relaxed resolution (as that of D17) was employed while measuring on the TOF reflectometer CRISP. This gives an example of measuring on reactor based instrument and that on TOF mode. The difference in the data with D17 and CRISP is basically due to their respective angular and wavelength resolutions in obtaining a relaxed Q-resolution for both that was chosen to increase the intensity.

For CRISP, though the drop in intensity is below 1×10^{-5} (five orders of magnitude), it suffers from large error bars (owing to the relaxed binning in TOF mode). On the other hand, the measured dynamical range remain small (as the intensity drops by 1×10^{-3}) for HADAS and for D17 (drops by 7×10^{-2}) which limits the information that can be retrieved from them (due to limited Q range).

We present the data from different reflectometers (for the first time) to show that the extraction of the data from various detectors by different means can bring some minor changes in the interpretation of the data. The respective differences in SLD profiles are nominal and do not affect the overall interpretation. The fits to the data are done with the same program, which indicates to the fact that the interpretations are not dependent upon data treatment. For practical purpose, data extraction from a 2d-detector (done in case of the HADAS data) or from a linear detector (as done in case of the ISIS data) can suffer from little discrepancies as well. This presents therefore a realistic scenario which cannot be ignored. If they were not measured at different sources and/or instruments this discrepancies would have been unnoticed.

B. Segregation and non-segregation model treatments

The data has been fitted considering a mixed layer of Ge, Fe, and Mn capped with another layer of ZnS. We employ here two different models for our fits. Model-1 (M_1) considers no

segregation of species (magnetic) on to the top cap layer while model-2 (M_2) considers a segregation of co-dopants in the DMS layer. Segregation of the DMS layer is identified by the movement of the magnetic species along the thickness of the sample. Such a segregation, on annealing, may lead to an inhomogeneous distribution of the species within the layer. However, it has been often observed that such a segregation which occurs particularly for the magnetic species, results in their movement to the top of the layer surface. Such segregated magnetic species are susceptible to form small clusters and act as independent magnetic regions. Thus they behave as isolated domains within the semiconductor matrix and cannot therefore be considered as a true DMS layer any more.

A homogeneous layer is characterized by a single magnetic phase (magnetization curve showing single transition temperature as in the case of DMS₄Fe₂Mn) while clustered species can lead to a second transition temperature (as in the case of DMS₂Fe₄Mn). Now as our specimens are covered with a cap-layer, it is likely that the magnetic species may even move into the cap-layer of ZnS. This is why we consider two different models for our simulations or fits where the ZnS layer is considered as non-magnetic in model-1 and as magnetic in model-2. In this way, by comparing the two situations for a single specimen, we would be able to identify any segregation in the sample.

The nuclear part (ρ_n) as well as the magnetic part (ρ_m) of SLD is considered as fitting parameters for model-2, as a segregation magnetic species would also alter the nuclear part of the SLD for both (cap and DMS) layers. This is done by keeping in mind of the typically observed 'phase problem' in neutron scattering which arises due to implicit phase information in the scattering terms from individual layers. As we rely on analyzing the data from a Fourier transform of the nuclear and magnetization profile, treating the data in such a way, would not only identify any segregation but also crosscheck our inference on the magnetization profile. The goodness of any fit is certainly depends upon the quality of the data. Thus if any modification of the layer characteristics (comparing the fits from M_1 and M_2) i) fails to improve the quality of the fit, then we may infer it as a case of no segregation into the cap-layer. ii) if the quality of the fit remains similar, then any inference drawn from the data would obviously be ambiguous. iii) On the other hand, if the quality of the fit is significantly improved, then the data (even within the limited range) can be considered as sensitive enough to identify such segregation.

Now we compare the fits to the data involving the two models M_1 and M_2 (note that

fits to the data in Figure 1 are shown for treatment with M_1 only). The fits in black and red lines, in Figure 2, corresponds to the treatment of the data without considering any chemical or magnetic variation with depth for the DMS layer (M_1). This is the case we start our least square fits by restricting the parameters to the situation where we consider the DMS layer to be homogeneous. The fitting parameters that are let free are the individual layer thicknesses, the nuclear part and magnetic part of the DMS layer SLD and the nuclear part of the cap-layer SLD. Note that the magnetic part of the cap layer (ρ_m) is restricted to zero in this model. The abruptness or smoothness of SLD profiles are dependent upon the number of slices one undertakes in the density profile during the fitting. The case presented here are to show that even with an abrupt profile the fits are reasonably good enough for our interpretation.

On the other hand, the fits in gray and cyan lines, consider DMS layer to segregate on to the top (M_2). In this case, we consider that the DMS layer is inhomogeneous and the magnetization observed, is due to the formation of isolated domains that may have crept into the ZnS layer. The restriction on the magnetic part of the cap-layer is now lifted and has been used as a fitting parameter, free to converge. The corresponding SLD variation in depth has been shown alongside of Figure 2. The SLD variation incorporates a variation in the nuclear as well as the magnetic part simultaneously.

C. Sample: DMS4Fe2Mn

We now look into the fits following M_1 . In this case, the ρ_n (black line) and ρ_m (red line) remains fairly similar for the data from the three reflectometers. Note the goodness of fit factor ($\chi^2 \approx 0.01$ (HADAS), 0.08 (D17) and 0.28 (CRISP)) for the respective data. Larger error bars in the CRISP data has lead to an increased χ^2 . However, similar SLD values have been obtained from the fits to the data from all the instruments (variation is around 5%). This is probably the first representation of similar data measured at different instruments.

On the other hand, if we look into the fits to the data following M_2 , the χ^2 remain very similar to that obtained with M_1 for the HADAS data with no real change in the fit parameters. Thus the HADAS data is considered as insensitive to any segregation of magnetic species. The D17 data on the other hand do show a considerable increase in the magnetic part of SLD but without any drastic change in the other free parameters and even

manages to attain a similar χ^2 . This is therefore a typical example of the fact that any depth-information from such data can lead to ambiguous results.

The fits to the CRISP data, do not allow much changes for the nuclear parts of the respective layers as they remain close to the fitted value as that has been obtained using M_1 . Even though the magnetic part of the ZnS layer shows some increase with respect to that in M_1 , the bad quality of the data at higher Q values (large error bars) does not permit any convincing interpretation and the χ^2 remains almost similar.

No improvement in χ^2 (rather worsen by ~ 0.07) is obtained for DMS4Fe2Mn when treated by M_1 and M_2 for the data set from TREFF. This implies that a segregation model (M_2) fails to improve the fit over non-segregation model (M_1) for DMS4Fe2Mn. Instead of a similar χ^2 (as in case of HADAS or CRISP data when treated with the two models), we found an increase in χ^2 while fitting within M_2 as compared to M_1 . This already strongly indicates the non-segregation in this specimen.

D. Sample: DMS2Fe4Mn

Within the M_1 model, the goodness of fit factors ($\chi^2 \approx 0.01$ (HADAS), 0.07 (D17) and 0.33 (CRISP)) for the respective data are given alongside the figures. The fits to the data from HADAS, D17 as well as from CRISP hardly show any significant difference with respect to DMS4Fe2Mn, expect for the relative changes in the nuclear and magnetic part of the SLD (here the variation of the fitted values on different instruments is around 7-10%). Even the respective χ^2 remains similar to the case of DMS4Fe2Mn.

Interestingly, when they are fitted with M_2 , the $\chi^2 (\approx 0.01$ (HADAS), 0.05 (D17) and 0.20 (CRISP)) is found to be somewhat lower (for D17 and CRISP). This in way indicates a validity for the segregated model. The HADAS data, however, remain similarly insensitive. The fits to the D17 data, which does not allow any drastic change of the nuclear part, shows some magnetic contribution throughout the depth of the layer thicknesses as the χ^2 is slightly reduced by (~ 0.02) as compared to the fits by M_1 .

Now let us focus onto the fits to the CRISP data. Here, similar to the case of DMS4Fe2Mn, the nuclear part remains almost similar to that obtained using M_1 . However, the corresponding magnetic part has attained a uniform distribution. This tendency, was also obtained from from D17 and in a way indicates to the fact that DMS2Fe4Mn is more susceptible to

segregate than DMS4Fe2Mn. The magnetization that was observed for DMS4Fe2Mn from SQUID, is therefore cannot be intrinsic to the DMS layer but, can be owed to the presence of segregated clusters. Our present results for DMS2Fe4Mn corroborate with previous measurements by TEM or SQUID on similar specimens^{5,6}.

This is further confirmed with the TREFF data as we find that for DMS2Fe4Mn, a clear improvement (improved by ~ 0.05) is achieved when M_2 is employed as compared to M_1 . Therefore, it can be concluded, that a sufficient level of segregation of magnetic species into the cap layer has taken place in DMS2Fe4Mn (inhomogeneities for higher Mn-doped specimens). While in DMS4Fe2Mn, no such segregation has been indicated by PNR, at least from the TREFF data (the data from HADAS, D17 and CRISP remain ambiguous).

From the measurements at various instruments, we realized that sensitive measurements are significantly determined by the angular resolution and the wavelength resolution that has been employed during the measurements in addition to the neutron flux at the sample position and the background level at the instrument. The HADAS data was measured with a relaxed angular resolution (3.5%) but with a restrained wavelength resolution (1.5%) and most importantly was also limited in its neutron flux. The D17 data, on the other hand, was rich in its neutron flux and was measured with a stricter (1.5%) angular resolution. However, the wavelength resolution was relaxed to $\sim 4\%$. Thus the overall Q resolution was relaxed to $\frac{\Delta Q}{Q} \approx 4\%$ for both measurements. Apparently such a resolution would have been sufficient in observing the differences in spin-asymmetry. However, such is not the case here, as the background level at the instruments was found unsatisfactory for such sensitive measurements. The CRISP data, on the other hand, had the advantage of high neutron flux and also lower background. However, the wavelength resolution was again relaxed to be around 3% which might have affected the overall Q resolution. The error bars in the CRISP data also contributed to its inconclusiveness. Comparing the CRISP data with that of others one may notice that the CRISP data has many more data points. A more aggressive rebinning would have reduced the magnitude of the error bars (reducing the number of data points at the same time), particularly at high Q.

It is quite evident from the fact that the fits to the data (HADAS, CRISP and D17) remain largely insensitive to the two different models (M_1 and M_2) employed for the two specimens. Although segregation model (M_2) apparently implied magnetic contribution within the cap-layer (see SLD variation from the D17 and CRISP data) for DMS2Fe4Mn

(lowering of χ^2), nothing conclusively can be inferred about segregation or non-segregation in these specimens. Thus, in addition to a high neutron flux, it was felt that a stricter Q resolution and a cleaner background are required for such challenging experiments. The spin-asymmetry signal is seen to die down at around $0.03\text{\AA}^{-1}$. One may note that we have made no corrections to the raw data and have incorporated the resolution functions and the background level into the fitting routine. In Figure 3 we plot the average values of extracted SLD profiles following model M_1 for DMS4Fe2Mn and model M_2 for DMS2Fe4Mn as obtained from the four instruments with minimum in χ^2 . The segregation into the cap layer (ZnS) for DMS2Fe4Mn can be distinctly observed from the TREFF data. The SLD values in ZnS layer show ferromagnetism in the layer though it is a little weaker than the case of TREFF. The TREFF data, on the other hand, indicates that the ZnS layer becomes ferromagnetic by the segregation of Mn and Fe atoms, the SLD of which is rather similar in average (almost within the error bar) to that in Ge-MnFe.

All the above factors were taken into account while measuring at TREFF. We show in Figure 4 the unpolarized data (measured with the same angular and wavelength resolutions as that for the polarized one) from the two specimens that clearly indicate of their high quality – needed for our measurements. The difference in their respective critical angles of total reflection does indicate different chemical compositions of the cap-layer and the shift of the Kiessig fringes indicates slightly different total thicknesses for the two specimens. Here the neutron flux was high, the wavelength resolution was restricted (similar to that at HADAS), the angular resolution was restricted (similar to that at D17) and the background level was also kept as low (close to that at CRISP) as possible. The overall Q resolution was restricted to $\frac{\Delta Q}{Q} \approx 2\%$. Even though this cannot be a strong reason for the observed differences in SLD values, we would like to draw the attention over the spin-asymmetry signal with Q. The spin asymmetry signal can be seen even around $0.06\text{\AA}^{-1}$ for TREFF as compared to $0.03\text{\AA}^{-1}$ for the other two angle-resolved instruments. We believe that all of these factors – in combination – have certainly assisted in a better estimation of the parameters particularly being able to observe a spin-asymmetry signal at a higher Q. Without the experience from the different reflectometers it would not have been possible to perform such a sensitive and challenging measurement. Variation of different instrumental parameters and conditions are certainly not expected within a single reflectometer. This also justifies our effort in measuring at different reflectometers in digging out a comparative depth

sensitive magnetic segregation from our DMS specimens. One must also remember here that retrieving the SLD profile from a measured data is restricted primarily by the phase problem as conventional reflectivity measures only $|r(Q)|^2$ of the complex reflection amplitude $r(Q)$ and suffers from general nonlinear dependence of measurements on the SLD.¹⁰ Thus even two different SLD's can simulate similar patterns or vice-versa. This is more significant in the low-Q regime where the Born approximation typically breaks down. With polarized beam, retrieving the profile becomes even more difficult due the additional magnetic parameters get involved along with halving the available intensity. However, methods that can be used, in principle, for determining the phase of reflection is beyond the scope of this paper.

We compare the fitted parameters from the two specimens as obtained from the PNR data. The average magnetic moment per magnetic atom (μ_m), estimated from the fitted values of ρ_m , are slightly different from different fit values. However, considering the average values from TREFF (and other instruments), assuming atomic density of magnetic species to be $0.19N_{Ge}$ and using the equation $\rho_m = N \frac{\mu_m}{\mu_B} 2.695 \times 10^{-6} \text{ nm}$ we arrive at the respective values of $0.07\mu_B$ (DMS4Fe2Mn) and $0.09\mu_B$ (DMS2Fe4Mn) per magnetic impurity atom respectively (here μ_B is the Bohr magneton). Here, the respective scattering length densities (Nb_m) are $1.35 \mu m^{-2}$ and $1.75 \mu m^{-2}$. The atomic density of the DMS layer can be approximated as the density of Ge ($=38 \text{ nm}^{-3}$) from where one can determine N ($=0.19 \times 38 = 7.22 \text{ nm}^{-3}$). Our calculations are in agreement with our magnetization data reported earlier⁶. For DMS4Fe2Mn, larger error bars in the data (CRISP) along with a lower effective magnetic moment, could not indicate of the inhomogeneities throughout the depth of the film. Recent theoretical calculations on similar systems have shown that the physics of magnetic interaction between the two different dopant magnetic species in Ge based systems, are in complete agreement with the findings of this paper¹⁴.

V. CONCLUSION

In conclusion, we present a comparison of the PNR data obtained from various instruments on different neutron sources in an effort to investigate the depth dependent segregation of magnetic species in co-doped DMS specimens. We find that PNR could effectively indicate of such segregation when the effective magnetization within the DMS layer (due to co-doped magnetic-ion concentration) is significant enough. Depth profiling for specimens

with even lower magnetization (due to alternate co-doping of magnetic-ion concentrations), is a challenge that can be overcome with the brightest sources available and with proper care of the overall Q resolution and a lower background level at the instrument. The samples investigated indicate no segregation and lower clustering tendencies for higher Fe co-doping.

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FIG. 1: (Color online) Measured (solid symbols) and fitted (open circle) NSF [R_{--} (black square) and R_{++} (red circle)] reflectivity patterns of "DMS4Fe2Mn" and "DMS2Fe4Mn" measured at saturating applied fields H_a and at 50 K. The earlier measurements from HADAS are also shown for comparison. The fits to the data are treated within the dynamical approach considering no segregation (model M_1) and uniform scattering length density of individual layers with thickness. No background subtraction or correction for polarizing efficiencies are done to the data as they are considered within the fitting routine.

FIG. 2: Comparison of the data recast as spin asymmetry (SA) for DMS4Fe2Mn (left panel) and DMS2Fe4Mn (right panel) measured at HADAS (red), D17 (green), CRISP (blue) and TREFF (magenta) at a saturation field and at 50 K. Also shown are the fits within the dynamical model M_1 and M_2 considering no segregation (black lines) or segregation (gray lines) respectively. Also shown are the corresponding SLD variation with depth, plotted in black/red (for no segregation) and gray/cyan (for segregation) lines.

FIG. 3: Plot of the average values of extracted SLD profiles following model M_1 for DMS4Fe2Mn and model M_2 for DMS2Fe4Mn as obtained from the four instruments.

FIG. 4: Measured unpolarized reflectivity patterns of "DMS4Fe2Mn" (solid circle) and "DMS2Fe4Mn" (solid square) measured at saturating applied fields and at room temperature.