Single ion anisotropy of Mn doped GaAs measured by EPR.

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Electron paramagnetic resonance (EPR) study of MBE grown Mn doped GaAs is presented. The resolved fine structure allows us to evaluate the crystal field parameters of the spin Hamiltonian. The obtained cubic constant is $a = -14.1 \cdot 10^{-4}$ cm$^{-1}$. The axial field parameter, $D$, increases with Mn concentration, $x$, i.e., with the strain of Ga$_{1-x}$Mn$_x$As layers. Extrapolation of $D$ shows that the single ion anisotropy is the important contribution to the magnetic anisotropy which is observed in ferromagnetic layers with greater Mn concentrations. The analysis of the EPR linewidth shows that native defects of the concentration of $5 \cdot 10^{19}$ cm$^{-3}$, but not the Mn ions, are the main origin of crystal field fluctuations.

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Ga$_{1-x}$Mn$_x$As is a semiconductor which exhibits ferromagnetic properties [3, 4]. It is one of the most promising diluted ferromagnets which can be applied in magnetic semiconductor devices. The ferromagnetic phase occurs already for $x \approx 0.02$ and for $x \approx 0.04$ the Curie temperature reaches 90 K. Some logic structures, where the magnetic phase is switched on by an electric gate have already been built [5].

Ferromagnetic layers grown by low temperature molecular beam epitaxy (MBE) exhibit an axial magnetic anisotropy which plays a crucial role in magnetic properties of Ga$_{1-x}$Mn$_x$As layers and multi layer structures. The sign of the anisotropy depends on the substrate. For a tensile strain the direction parallel to the growth direction is the easy axis while for compressive strain the easy direction lies in the grown plane. The magnitude of the anisotropy field is of the order of 5-50 mT. Definitely, the anisotropy does not originate from magnetic dipole interactions. Such a shape anisotropy should be by an order of magnitude smaller and the easy axis would have to lie in plane. The complex nature of the valence band structure leads us to expect pseudo-dipole or Dzialoshynski-Moriya interactions [6]. They could lead to a broadening of the resonance linewidth but their theoretical estimations is not simple. To distinguish whether the anisotropy originates from a single ion anisotropy of Mn$^{2+}$ ion or from a non Heisenberg exchange coupling between Mn$^{2+}$ ions we have undertaken a detailed electron paramagnetic resonance (EPR) study of Mn in MBE grown Ga$_{1-x}$Mn$_x$As.

Some reports on EPR of Ga$_{1-x}$Mn$_x$As were already published [6, 7]. The hyperfine structure (HFS) is commonly observed but the fine structure (FS) of the EPR spectrum has not been resolved until now. Almeleh and Goldstein estimated the upper limit of the cubic component of the crystal field parameter, $a$, in bulk samples [8]. The axial crystal field component, described by the parameter $D$, which may occur in strained structures only, has not yet been analyzed. In this paper we present EPR studies of weakly doped Ga$_{1-x}$Mn$_x$As compounds growth by MBE. We are able to find a resolved FS and to evaluate the single ion anisotropy and fluctuations of the crystal strain. No broadening of EPR lines caused by non-Heisenberg component of Mn-Mn coupling has been found.

The samples were grown by low temperature molecular beam epitaxy (LT MBE) in a KRYOVAK MBE system [8]. The calibration of Ga and Mn sources allows us to estimate the Mn content with an accuracy better than 0.1%. The composition of samples with low Mn concentrations was verified by SIMS measurements and by the integrated amplitude of EPR signal. The thickness of low concentration samples was about 2 micrometers. The XRD measurements showed that all samples with Mn content from $10^{-5}$ to $10^{-3}$ are coherently strained by the GaAs(100) substrate.

In EPR studies we found that samples with $x \leq 1.5 \cdot 10^{-3}$ are characterized by a well resolved HFS and some weakly resolved FS. For $x > 2.5 \cdot 10^{-3}$ only a single broad line is observed. The spectra of Ga$_{1-x}$Mn$_x$As ($x = 4 \cdot 10^{-4}$) for four various directions of the applied magnetic field are shown in Fig. 1. The magnetic field was applied in the (110) crystal plane and $\Theta$ is the angle measured from the [001] direction.

These spectra are characterized by $g = 2$ and definitely originate from $S = 5/2$ of Mn$^{2+}$ ions. Schneider et al. found additional lines of a neutral acceptor with $g = 2.77$ [9]. We observe only the signal of ionized acceptors which indicates that LT MBE samples are strongly compensated.
The dependence of the spectrum on the magnetic field of Mn, are well resolved for an arbitrary direction of the magnetic anisotropy. The corresponding anisotropy field for ferromagnetically saturated spins is \( \delta H = g \mu_B H / (g \mu_B + A S I) \), where \( g \) is the Bohr magneton. The second term corresponds to the HFS coupling which is assumed to be isotropic. The third and the fourth terms describe the FS structure, corresponding to the axial and the cubic symmetry of the crystal field, respectively. The parameter \( D \) is directly related to the single ion contribution to the magnetic anisotropy. The corresponding anisotropy field for ferromagnetically saturated spins is \( H_A = SD / g \mu_B \).

The positions of 30 spectral lines, corresponding to six orientations of the nuclear spin, \( I \), \( (M_I = -5/2, \ldots, 5/2) \) and to five different spin flip transitions between six energy levels labeled by \( M_S \) \( (M_S = -3/2, \ldots, 5/2) \) were calculated according to spin Hamiltonian (1). To evaluate the spin Hamiltonian parameters we took the best fit of all spectra measured for various field orientations \( \Theta \). Details of the fitting procedure is discussed below. The best fit was obtained for \( |\alpha| = (14.1 \pm 0.3) \cdot 10^{-4} \) cm\(^{-1}\). Within the experimental error this value does not depend on the Mn concentration, \( x \). The value of the axial component of the crystal field, \( D \), is much smaller than the cubic parameter, \( a \). For the data shown in Fig. 1, \( D = (1.3 \pm 0.02) \cdot 10^{-4} \) cm\(^{-1}\). The dependence \( D \) on \( x \) is shown in Fig. 2.

Because the line broadening is mainly due to super HFS caused by the coupling of Mn\(^{2+} \) spins with the nuclear spins of the ligands, the shape of the individual spectral lines is assumed to be described by a Gaussian function which gives a much better fit as compared to the Lorentz line shapes assumed. The satellite lines are characterized by a slightly bigger linewidth. In the fitting procedure we used two parameters describing the width of individual spectral lines: the linewidth of the central FS line, \( \Delta H_{1/2,-1/2} \), and the parameter describing an extra broadening of the satellite lines of FS: \( \delta \Delta H = \Delta H_{5/2,3/2} - \Delta H_{1/2,-1/2} \). The width of the line \( (3/2,1/2) \) is assumed to be equal to the mean value: \( \Delta H_{3/2,1/2} = (\Delta H_{5/2,3/2} + \Delta H_{1/2,-1/2}) / 2 \). The best fitted value of the linewidth is \( \Delta H_{1/2,-1/2} = (2.0 \pm 0.02) \) mT. It is found to be isotropic and independent of \( x \). The additional broadening of the satellite lines, \( \delta \Delta H \), is a small effect. For the data shown in Fig. 1, \( \delta \Delta H = 0.4 \) mT. This corresponds to a fluctuation of \( D \), \( \delta D = \delta \Delta H / g \mu_B \), equal to \( 2 \cdot 10^{-4} \) cm\(^{-1}\). As it is shown in Fig. 2b this value varies from sample to sample by about 40% but there is no systematic variation of \( \delta \Delta H \) with Mn concentration.

The resolved FS and HFS vanish with the increase of Mn concentration. To simulate the observed shape of the EPR spectrum it is not enough to consider the broadening of the individual spectral lines. A good fit is obtained only when we treat the spectrum as a sum of the resolved one, originating from individual, non interacting Mn\(^{2+} \) spins, and the unresolved contributions with averaged FS and HFS. With an increase of \( x \) the width of individual lines of the resolved spectrum \( (\Delta H_{1/2,-1/2} \) and \( \delta \Delta H \) practicallly does not change. The resolved structure gradually disappears because of the decrease of the amplitude of the resolved contribution. For low \( x \) the width of the unresolved contribution corresponds to the second moment of the spectrum of non interacting Mn\(^{2+} \) spins. With a concentration increase a decrease of the width of the unresolved spectrum is observed. We relate this decrease to the exchange narrowing effect.
Anisotropy in ferromagnetic Ga$_{1-x}$Mn$_x$As, the total magnetic anisotropy of ferromagnetic layers. Single ion anisotropy is the considerable contribution to the coercive field observed in ferromagnetic samples [2,10]. It allows us to conclude that the axial component of the crystal field anisotropy, $D$, is caused by a local strain acting on the ion. It increases with an increase of $x$. The data shown in Fig. 2 can be approximated by a linear dependence $D = (0.09 \cdot x + 1.05 \cdot 10^{-4})$ cm$^{-1}$. The value $DS/\mu_B$ corresponds to the single ion contribution to the total anisotropy field (when a saturated polarization of Mn spins is assumed). For $x = 1.5 \cdot 10^{-3}$ the anisotropy field is $DS/\mu_B = 0.7$ mT. However, since the layer strain increases linearly with $x$, the single ion anisotropy expected for $x = 0.035$ is $DS/\mu_B \approx 10$ mT. This value agrees well with the coercive field observed in ferromagnetic samples [2,10]. It allows us to conclude that the single ion anisotropy is the considerable contribution to the total magnetic anisotropy of ferromagnetic layers.

The fact that the extrapolation of the parameter $D$ to low Mn concentration, $x \to 0$, does not tend to zero we relate to an additional strain which appears at low temperature caused by a difference of the thermal expansion coefficients of Ga$_{1-x}$Mn$_x$As, GaAs and sample holder.

The signs of the parameters $D$ and $a$ cannot be directly determined from EPR measurement. The data allow only to conclude that the parameters are of opposite sign, $a \cdot D < 0$. However, from the fact that the magnetic anisotropy in ferromagnetic Ga$_{1-x}$Mn$_x$As layers grown on GaAs substrate shows an easy in-plane magnetization, we conclude that $D > 0$, and, in consequence, we suggest that $a < 0$.

Within the whole range of composition where the EPR spectrum is well resolved the linewidth of the central FS line, $\Delta H_{1/2}$, is constant. Up to $x = 1.5 \cdot 10^{-3}$ we do not observe any additional broadening of the resolved part of the spectrum which could be attributed to dipole or pseudo-dipole (non-Heisenberg exchange coupling) interactions. The resolved part of the EPR spectrum, however, does not originate from a statistic Mn spin but from those Mn ions which do not have any other Mn ion in the neighborhood. Because of that we are not able to conclude about the magnitude of a mean dipole or pseudo-dipole coupling between Mn ions. Moreover, the discussed samples are strongly compensated. Because of that the fact that no effect of non-Heisenberg Mn-Mn coupling has been found does not allow us to made any solid conclusion about the character of RKKY interactions.

The additional broadening of the satellite lines of FS, $\delta \Delta H_s$, can be attributed to fluctuations of the local strain. Because the position of the central FS line is not affected by crystal field, the strain induced fluctuations of FS structure parameters, $a$ and $D$ (including a random direction of the local strain), do not affect the width of the central FS line, $\Delta H_{1/2}$. However, they lead to a broadening of the satellite lines only. Consequently, $\delta \Delta H_s$ scales the amplitude of the strain fluctuation. Assuming that the evaluated derivative $dD/dx = 0.09$ cm$^{-1}$ (see Fig. 2) is directly related to the difference of the lattice constants between Ga$_{1-x}$Mn$_x$As and the GaAs substrate, one can estimate fluctuations of the deformation of the crystal cell, $a$, in the vicinity of Mn dopant caused by other impurities to be $\delta a_0 = 10^{-4}a_0$. This value is considerably bigger than the mean fluctuations amplitude as measured by rocking curve of XRD. The fact that $\delta a_0$ is independent of $x$ indicates that the fluctuations, $\delta a_0$, do not originate from neighboring Mn ions but from other, non magnetic defects, probably antisites.

Concluding, the single ion anisotropy caused by the layer strain is an important contribution to the whole magnetic anisotropy observed in ferromagnetic Ga$_{1-x}$Mn$_x$As layers. Discussion of the local strain, as measured by broadening of the satellite lines of FS, $\delta \Delta H_s$, allows to estimate crystal strain fluctuations. The independence of the crystal field fluctuations, of $x$ indicates that the concentration of native defects is independent of the Mn content. Assuming that the range of $x$ where the well resolved EPR spectrum of ionized Mn acceptors is observed corresponds to the range of insulating and fully compensated crystal, the upper limit of this range, $x = 2.5 \cdot 10^{-3}$, allows to estimate the concentration of compensating centers to be $5 \cdot 10^{19}$ cm$^{-3}$.

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