Magnetic-moment formation of Fe and Mn in crystalline and amorphous Ga: An *in situ* low-temperature ion-implantation study

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Low-temperature ($T < 10$ K) ion implantation of Fe and Mn is applied to produce metastable random solutions of these impurities in crystalline β-Ga and amorphous (a-) Ga films. Because of their restricted stability (a-Ga < 17 K, β-Ga < 65 K), the Ga-host phases have to be prepared by quenching techniques *in situ*. Using the concentration dependence of the superconducting transition temperature as a probe for the magnetic behavior it is found that only Mn forms a long-lived magnetic moment in both Ga modifications, while the results for Fe are consistent with a rapidly fluctuating short-lived moment.

The question of whether a $3d$ impurity like Fe or Mn possesses a stable local magnetic moment within a metallic host has found renewed interest during the past years due to progress of theoretical as well as experimental techniques. The theoretical description of the local magnetic moment formation in a metal host, pioneered by Friedel and Anderson,[1,2] has meanwhile developed to a level allowing quantitative predictions. These achievements are mainly based on spin-dependent density-functional or Green's-function formalisms.[3–6]. A recent example is the work of Guenzburger and Ellis,[7] who demonstrated that a vanishing moment of an Fe impurity within Al can only be obtained theoretically if the local lattice relaxation around the Fe is taken into account. This result provides evidence that the local environment around the impurity plays a crucial role in moment formation.

Experimentally, one faces the difficulty of keeping the impurity concentration low enough to stay within the single-impurity limit (i.e., impurity-impurity interactions can be neglected), leading to the demand for a highly sensitive technique. In simple metals like Ga, the additional problem arises that the equilibrium solubility of Fe and Mn is virtually zero. Thus, to avoid small impurity precipitates, metastable solid solutions have to be prepared. One way to overcome the solubility problem is to apply nuclear techniques,[8] which are sensitive to impurity concentrations below the ppm level. But here, the number of possible impurity candidates is restricted. As an important example, Mn impurities cannot be produced in this way. Nevertheless, this technique has been very successfully applied,[8–10] and Riegel *et al.* have performed a systematic series of measurements using this method to study the moment formation of Fe in *sp*-band metal hosts.[11] They concluded that Fe is nonmagnetic in small-volume *sp* metal hosts like in Ga with high accuracy.

In the present work a totally different experimental approach has been adopted, allowing us also to study Mn impurities. Magnetic ions were implanted into thin Ga films (typical thickness 40 nm) at temperatures ($T < 10$ K) low enough to inhibit impurity diffusion. In this way a metastable random distribution of the impurities within the metal host is prepared and their concentration can be continuously increased (ppm steps) within the same film. The magnetic behavior of the impurities is then monitored *in situ* at $T < 10$ K by using the superconducting transition temperature T_c as a probe. The more direct possibility of probing the magnetic moments by measuring the temperature dependence of the susceptibility using a superconducting quantum interference device (SQUID) magnetometer is hindered by the demand to detect a small total number of paramagnetic moments within a thin film and to combine it with an *in situ* low-temperature preparation and implantation technique. The T_c method relies on the fact that magnetic moments always result in a T_c decrease. Different theories have been developed for the concentration dependence of the T_c decrease, all resulting in a linear relation initially for small concentrations. A summary has been given by Maple,[12] who also defines and distinguishes between "long-lived" and "rapidly fluctuating" magnetic moments, which are theoretically described by different approaches.[13–15] In the following we use these terms accordingly.

The *sp* metal Ga was chosen for the following reasons: Ga is one of the few metallic elements which can be forced into a metastable amorphous phase (a-Ga) without adding a second stabilizing species by quenching its vapor onto liquid-helium-cooled substrates[16] or, alternatively, by bombarding the equilibrium orthorhombic α-Ga phase with heavy ions, e.g., Ar^+ at $T < 10$ K.[17] The amorphous phase exhibits a rather high transition temperature with typical values between 8.1 and 8.4 K, but its stability is restricted to $T \leq 17$ K. Above this temperature a-Ga irreversibly transforms into the metastable crystalline (monoclinic) β phase.[16,17]

This β-Ga phase shows a transition temperature of $T_c = 6.3$ K and is stable up to $T = 65$ K. At this temperature β-Ga transforms into the equilibrium α-Ga phase with $T_c = 1.07$ K. Thus, Ga offers the chance to study the effect of missing long-range order on the local moment formation under chemically well-defined conditions. This was the main topic of the present work and therefore all experiments were performed on amorphous Ga and crystalline β-Ga (the low T_c value of α-Ga inhibited experiments on this phase in our cryostat). Furthermore, due to the metastability of the studied Ga phases, the present work, to our knowledge, is the first study on magnetic moment formation within these systems.

The effect of radiation damage on the superconducting transition temperature has to be determined separately. In the present case this is done by ion irradiating Ga films with nonmagnetic chemically inert ions (Ne^+,Ar^+,Kr^+). The experimental procedure is as follows: amorphous Ga films (40 nm thick) are prepared by vapor quenching onto lHe-cooled substrates or by ion bombardment of α-Ga films (40 nm thick) at $T<10$ K. These a-Ga films are then irradiated at $T<10$ K with 230-keV Ar^+ ions and the corresponding T_c changes ΔT_c are measured. The projected range of the Ar projectiles as calculated by the Monte Carlo code TRIM (Ref. 18) is 140 nm, with a straggling of 65 nm. Thus, effects of Ar implantation into the Ga films can be neglected. To allow an accurate determination of the small ΔT_c values only one-half of the Ga films is bombarded and T_c is measured for both the irradiated and unirradiated part. In this way, the relative shift of T_c can be obtained with high accuracy. The results of such experiments are shown in Fig. 1(a), where ΔT_c of a-Ga films is plotted versus the average energy deposited by the projectiles into the films per host atom (Q_D) via nuclear collisions as calculated by TRIM. This parameter is proportional to the ion fluence Φ (ions/cm^2) and allows a comparsion of the effect of different projectiles. The open symbols in Fig. 1(a) represent the results for amorphous films prepared by ion irradiation, the closed symbols those obtained for quench-condensed films. The important conclusion from these data is that radiation damage leads to linear T_c decrease of a-Ga films with a slope of -0.5 mK/eV [dashed and solid lines in Fig. 1(a)]. The corresponding results for β-Ga films (40 nm thick) obtained by crystallization from the amorphous phase are shown in Fig. 1(b). In this case, for all three types of projectiles (230-keV Ne^+, 275-keV Ar^+, 350-keV Kr^+) a linear T_c increase of the order of $+1.1$ mK/eV is observed due to radiation damage. The behavior given in Fig. 1 must be compared to the following data obtained by implanting magnetic ions into different Ga phases. Figure 2 shows the results for implanting Fe^+(35-keV) and Mn^+(40-keV) ions into amorphous Ga films (40 nm thick) at $T<10$ K. The corresponding calculated Gaussian implantation profiles of the magnetic impurities are centered in the middle of the Ga films ($R_{p,\mathrm{Mn}}=22$ nm, $R_{p,\mathrm{Fe}}=20$ nm) and the range stragglings ΔR_p are large enough ($\Delta R_{p,\mathrm{Mn}}=13$ nm, $\Delta R_{p,\mathrm{Fe}}=11$ mn) to guarantee quite homogeneous depth distributions. The concentrations given in Fig. 2 are the peak values of the implantation profiles. Clearly, both Mn and Fe impurities lead to a linear T_c decrease (solid lines), with Mn exhibiting a larger slope of -3.4 K /at. % as compared to Fe at -1.3 K/at. %. The observed linearity provides evidence that for concentrations below 500 ppm a single impurity regime can be assumed. The fact that the solid lines in Fig. 2 extrapolate back to a finite ΔT_c value (<50 mK) for $c_{\mathrm{imp}}=0$ can be explained by structural rearrangements of the amorphous phase due to the change of projectiles from Ar^+ (used for amorphization) to Mn^+ or Fe^+, which always results in a small T_c increase. This effect of different types of structural disorder on T_c has been recently discussed in detail for a number of sp metals, including Ga.[19]

In order to decide whether the observed T_c depression can be attributed to magnetic moments of the implanted impurities, the effect of the accompanying radiation damage must be taken into account. The results of such an analysis are presented in Fig. 3, where the experimentally observed T_c changes are plotted versus the calculated[18] energies Q_D deposited by the different projectiles into the Ga films via nuclear collisions. The significantly larger

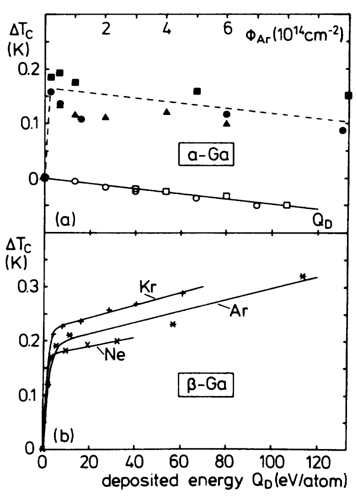

FIG. 1. Irradiation-induced changes of the superconducting transition temperature ΔT_c vs the mean energy Q_D deposited within the sample via nuclear collisions per host atom. In all cases the projected range of the inhert ions is larger than the film thickness. (a) Ar^+ irradiation (230 keV) of amorphous Ga films. Closed symbols: different films prepared by vapor quenching onto lHe-cooled substrates. Open symbols: amorphous films prepared by low-temperature Ar^+ irradiation of α-Ga films. (b) Irradiation of crystalline β-Ga films with 230-keV Ne^+, 275-keV Ar^+, and 350-keV Kr^+ as indicated in the figure.

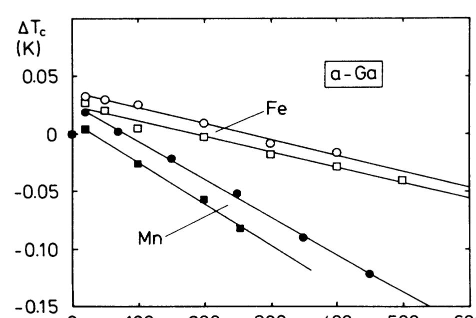

FIG. 2. Changes of the superconducting transition temperature ΔT_c produced by low-temperature ($T<10$ K) Fe^+ (35 keV, open symbols) and Mn^+ (40 keV, closed symbols) implantation into amorphous Ga films as a function of the impurity concentration.

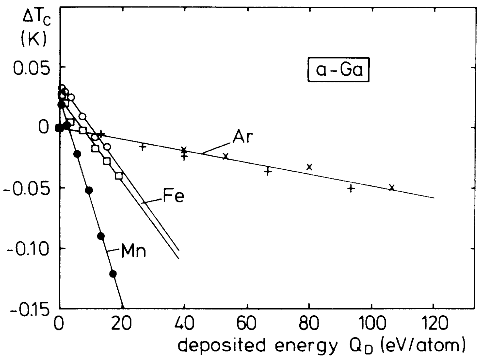

FIG. 3. Changes of the superconducting transition temperature ΔT_c as a function of the mean energy Q_D deposited within the amorphous Ga films via nuclear collisions accompanying the impurity implantation. The Ar irradiation data (crosses) serves as a reference for the effect of pure radiation damage.

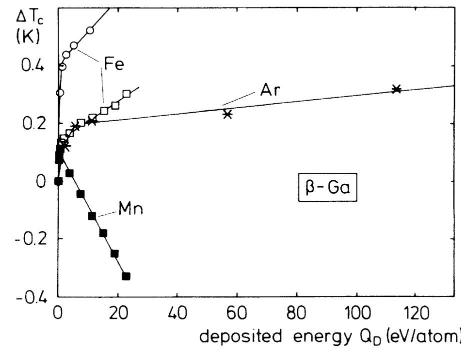

FIG. 5. Changes of the superconducting transition temperature ΔT_c as a function of the mean energy Q_D deposited within crystalline β-Ga films via nuclear collisions accompanying the impurity implantation. The Ar data serve as a reference for the effect of pure radiation damage.

T_c depression found for Mn (-8.9 mK/eV) and Fe (-3.5 mK/eV), as compared to the Ar irradiation (-0.5 mK/eV) where the T_c decrease is due to pure radiation damage, provides clear evidence for a magnetic effect. It is worth noting that in contrast to crystalline hosts, in the present amorphous case possible different lattice sites of the implanted impurities cannot be distinguished. Both types of impurities come to rest at the same average amorphous local environment.

To study the influence of long-range order and/or density on the magnetic behavior of Fe and Mn in Ga, the same type of experiments as above were performed on crystalline β-Ga. The effect of the implanted impurities on T_c as a function of their concentration is presented in Fig. 4. In contrast to the amorphous case (cf. Fig. 2), only Mn implantation leads to a linear T_c depression (-7 K/at. %, i.e., twice as large as in a-Ga), while Fe implantation results in a linear T_c increase ($+2.9$ K/at. %) within the experimental concentration range. As in a-Ga, extrapolation of the solid lines in Fig. 4 to $c_{\text{imp}}=0$ gives a finite ΔT_c value even though the β-Ga films were preirradiated with 3×10^{14} cm^{-2} Ar^+ ions (310 keV) to

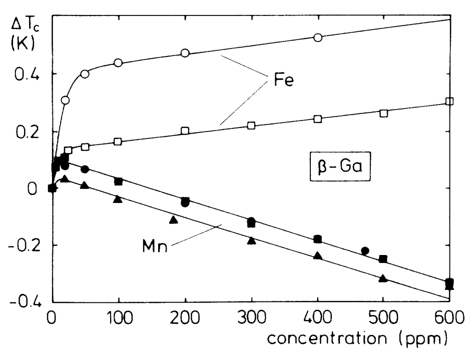

FIG. 4. Changes of the superconducting transition temperature ΔT_c produced by low-temperature ($T<10$ K) Fe^+ (35 keV) and Mn^+ (40 keV) implantation into crystalline β-Ga films as a function of the impurity concentrations.

saturate the radiation damage prior to the impurity implantation. Obviously, the change of projectiles leads to structural rearrangements resulting in positive ΔT_c values. Comparison to the effect of pure radiation damage is performed in Fig. 5, where ΔT_c is plotted versus the deposited collisional energy Q_D for the different projectiles. Since in β-Ga pure radiation damage produces a T_c increase ($+1.1$ mK/eV as given by the Ar data), only the observed T_c depression by Mn impurities allows the conclusion on a magnetic effect. In the case of Fe, the observation of a large T_c increase ($+7.5$ mK/eV) rather suggests an enhancement of radiation damage chemically stabilized by the implanted impurity. Alternatively, a different lattice site of Fe as compared to Mn cannot definitely be excluded, although the close similarity of the Z number and the mass of both impurities should lead to a similar ballistic behavior within the collision cascades, making an identical final site for both species highly probable.

Thus, we observe magnetic effects in three cases: (1) Fe in a-Ga, (2) Mn in a-Ga, (3) Mn in β-Ga with increasing T_c depressions from (1) to (3). The question remains whether these effects can be attributed to long-lived local magnetic moments of the impurities. We first discuss Fe in a-Ga. Based on Kaiser's theory[14] for pair weakening by rapidly fluctuating magnetic moments as given in Ref. 12, one can calculate the initial T_c decrease $(dT_c/dc)=-1$ K/at. %. To obtain this value, the following input data were used: the density of states per spin at the Fermi energy $N(E_F)_{\text{Ga}}=0.14$ eV^{-1},[11] the density of states for impurity d electrons $N_d(E_F)_{\text{GaFe}}=0.93$ eV^{-1},[20] the intra-atomic Coulomb repulsion $U_{\text{eff}}=1.5$ eV,[20] and the superconducting BCS-coupling constant for a-Ga $N(E_F)V=3.8$. Even in the nonmagnetic case, with $U_{\text{eff}}=0$, Zuckermann's dilution effect[15] describing the scattering of conduction electrons into $3d$-impurity states leads to a T_c depression of $(dT_c/dc)=-0.7$ K/at. %. The agreement of these theoretical values with $(dT_c/dc)=-1.3$ K/at. % as found by experiment leads us to the conclusion that Fe impurities neither in amorphous Ga nor in crystalline β-Ga possess a long-lived magnetic moment in accordance with the observations by Riegel *et al.*[11] for Fe in crystalline α-Ga. In contrast, the T_c depression $(dT_c/dc)=-3.4$ K/at. % for Mn in a-Ga is signficantly larger than the above values for fluctuating moments. The conclusion that Mn possesses a long-lived moment in a-Ga, though physically not unequivocal, is supported by earlier susceptibility measurements of Mn in *liquid* Ga,[20,21] which clearly revealed a long-lived moment. Thus our findings are in accordance with the interpretation of the amorphous phase as the frozen-in melt. The strongest T_c depression $(dT_c/dc)=-7$ K/at. % is observed for Mn in β-Ga. This value is probably a lower bound. If one assumes that Mn atoms can chemically stabilize radiation damage as do Fe atoms, leading to a superposed T_c increase (2.9 K/at. %), the upper bound of the T_c depression can be estimated as $(dT_c/dc)=-9.9$ K/at. %, which again is attributed to a long-lived magnetic moment. Since the densities of a-Ga and β-Ga are identical (6.2 g/cm^3 for both phases), the different observed T_c depressions of Mn in these phases have to be ascribed to different local environments around the impurity or to band-structure effects caused by the long-range order of β-Ga.

In summary, by combining low-temperature ion implantation ($T<10$ K) with *in situ* measurements of the superconducting transition temperature, the magnetic behavior of Mn and Fe impurities in metastable amorphous and crystalline Ga films (a-Ga and β-Ga) could be studied. From the results it is concluded that only Mn exhibits a long-lived magnetic moment in both Ga modifications.

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