Effect of magnetic Gd impurities on superconductivity in MoGe films with different thickness and morphology

Hyunjeong Kim, Anil Ghimire, Shirin Jamali, Thaddee K. Djidjou, Jordan M. Gerton, and A. Rogachev
Department of Physics and Astronomy, University of Utah, Salt Lake City, Utah 84112, USA
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We studied the effect of magnetic doping with Gd atoms on the superconducting properties of amorphous Mo$_{70}$Ge$_{30}$ films. We observed that in uniform films deposited on amorphous Ge, the pair-breaking strength per impurity strongly decreases with film thickness initially and saturates at a finite value in films with thickness below the spin-orbit scattering length. The variation is likely caused by surface induced magnetic anisotropy and is consistent with the fermionic mechanism of superconductivity suppression. In thin films deposited on SiN the pair-breaking strength becomes zero. Possible reasons for this anomalous response are discussed. The morphological distinctions between the films of the two types were identified using atomic force microscopy with a carbon nanotube tip.

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Understanding physical processes related to localized magnetic moments is particularly important for low-dimensional systems since such moments can form spontaneously on surfaces and interfaces of nominally non-magnetic materials. The formation of localized magnetic moments is well known in semiconductor heterostructures and devices, where they are carried by structural defects with unpaired electrons \[1\]. Localized magnetic moments were recently detected on the surface of a normal metal \[2\]: in superconducting systems, they are believed to be responsible for several unusual effects such as 1/f noise in SQUIDs and qubits \[3\] and an anomalous magnetic field enhancement of a critical current in nanowires \[4\]. The origin of spontaneously formed magnetic moments often remains unknown; on the other hand, their effects can be probed by magnetic moments that are introduced intentionally.

Here we study the effect of intentional magnetic doping on transport properties of ultra-thin MoGe films that undergo a superconductor–insulator transition (SIT) \[5–10\]. The mechanism of the SIT remains an important unresolved problem in condensed matter physics. In general, there are several distinct physical processes that may lead to the SIT. Within the fermionic mechanism, Cooper pairing is locally suppressed by disorder-enhanced electron-electron repulsion \[11, 12\]. The fermionic theories predict that the pair-breaking strength of magnetic impurities does not change with increasing disorder or decreasing film thickness \[13, 14\]. Experimentally, magnetic doping was studied in quench-condensed Pb \[15\] and Pb-Bi films \[16\]. In the latter case, behavior consistent with the fermionic theory was observed relatively far from the SIT. Several bosonic mechanisms were proposed for the critical regime of the SIT. In these models, Cooper pairs are preserved across the transition but coherence in the films is lost due to vortex proliferation \[17\], disorder-induced Cooper pair localization \[18, 19\], or fluctuations of the superfluid order parameter \[20\]. While the models cited in Ref. \[18, 21\] differ in their detail microscopic mechanisms, they all predict the appearance of a spatially inhomogeneous superconducting state. The emergence of this state was observed in numerical simulations \[21\] and was recently detected experimentally \[22\]. Possible effects of magnetic pair-breaking within the bosonic models have not yet been analyzed theoretically.

The amorphous MoGe system is particular suitable for studying magnetic doping. This is the only known system where suppression of the critical temperature can be explained by the fermionic theory in all range of films thicknesses. Moreover, this can be achieved with the constrained theory, which assumes that effective electron-phonon coupling is not affected by disorder or film thickness. MoGe films with this property need to be deposited on a substrate covered with an underlayer of amorphous Ge that helps to maintain constant bulk resistivity of the film and ensures its homogeneity \[23\]. On the other hand, a missing Ge underlayer makes it possible to obtain and test an inhomogeneous superconducting state. We selected Gd as a magnetic dopant because its magnetic moment is carried by a half-filled f-shell and does not depend on the host material.

The critical temperature of amorphous Mo$_x$Ge$_{100-x}$ alloys depends on the particular value of $x$. In the first stage of our study, we used co-sputtering from three independently controlled guns with Mo, Ge, and Gd targets to fabricate a series of thick Mo$_x$Ge$_{100-x}$-Gd films with varying Gd content and $x$ in the range 50-80 at. %. From transport measurements on these films we found that the alloy with $x \approx 70$ is the most suitable for the Gd doping. In this alloy the superconductivity is completely suppressed when 6.5 at. % of Gd is added; at lower Gd content we detected a single-step superconducting transition in $R(T)$ curves.

We fabricated two series of Mo$_{70}$Ge$_{30}$ films. Films of the A-series were deposited on a Si substrate covered with
a 60-nm thick layer of SiN grown by chemical vacuum deposition. For the B-series, prior to the deposition of MoGe film, a 3-nm thick underlayer of amorphous Ge was deposited. For oxidation protection the films of both series were covered by a 3-nm thick layer of Ge.

In Fig. 1A, we show the temperature dependence of the sheet resistance for undoped Mo$_{70}$Ge$_{30}$ films deposited on SiN (A-series). Within the studied temperature range (down to 0.3 K) the system undergoes a direct SIT with no intermediate metallic phase. As shown in Fig. 1C, in the insulating regime, conductance has the logarithmic temperature correction arising due to the weak localization and electron-electron interaction contributions. Qualitatively similar suppression of superconductivity was observed for films deposited on Ge underlayer. Figure 1B shows the mean-field $T_c$ (defined at the middle of the transition) as a function of sheet resistance for the two series of films. As expected we found that the $T_c$ for the B-series can be well fitted by the fermionic model. However the $T_c$ of the A-series deviates from the model for the films with thickness below 1.5 nm. It is interesting to note that the critical sheet resistance of the A-series ($\approx 5$ k$\Omega$) is close to the universal sheet resistance $R_q = h/4e^2 = 6.45$ k$\Omega$ predicted within the “dirty boson” model. The difference between A- and B-series cannot be explained by change in the dielectric constant of the substrate. SiN has lower dielectric constant than $\alpha$-Ge; therefore, electron-electron interactions in this system have worse screening and suppression of $T_c$ would be expected at lower values of sheet resistance than in B-series.

Looking for a possible structural effect of the Ge underlayer, we inspected surface morphology of several
FIG. 3: (A) 3D atomic force microscopy image of the surface of 1-nm thick MoGe film deposited on SiN (A-type). (B) 3D AFM image of a similar film deposited on SiN covered with 3-nm thick Ge underlayer (B-type). (C) The difference ΔA between the 1D Fourier profiles of the AFM images, normalized by the average profile, A, for the A-type and B-type films.

test samples with an atomic force microscope (AFM) equipped with a carbon nanotube tip that provided 2 nm lateral resolution. Typical 2D images are shown in Fig. 2A,B and 3D AFM images in Fig 3A,B. To extract quantitative information about the lateral scale of the topographical features, a spatial Fourier transform was performed on the AFM data. To reduce noise, the resulting data were averaged over different directions in Fourier space, yielding a 1D profile of A vs. k for both the SiN and Ge underlayer samples. In Fig. 3C we show the difference between the 1D Fourier profiles of the A-type and B-type films shown in Fig. 3A and Fig. 3B, normalized to the average of the A-type and B-type profiles.

The overabundance of intermediate spatial frequencies for the type-A sample indicates that the Ge underlayer smooths the surface and suppresses topographical features with a characteristic lateral scale of about 15 nm. This smoothing of the surface is also evident in comparing the AFM images. On the other hand, the average surface roughness, which characterizes the height of the topographical features, is 0.4–0.5 nm for both A-type and B-type films. Evidently, the missing Ge underlayer introduces inhomogeneities that are not strong enough to form a granular structure. This is also evident from transport measurements. We see from Fig. 1A that even for thinnest films the superconducting transition remains sharp with a well-defined T_c. There is no tail in R(T) as it is typically observed in granular materials [25]. Normal state properties of the films also do not indicate the presence of strong inhomogeneities. From the theory of weak localization (eq. 4.47a in Ref. 24) we estimated that the dephasing length L_ϕ at T=0.3 K is about 80 nm for our least resistive insulating film. Since we do not see any sign of the insulating behavior down to T=0.3 K, the one-electron localization length in our films should be larger (probably much larger) than 80 nm and thus cover many random “hills” and “valleys” of the films’ morphological profile.

The inset to Fig. 4A shows an arrangement of samples and targets used for fabrication of the MoGe films doped with Gd. The deposition was carried out by co-sputtering from two guns. Several substrates were positioned approximately at the same distance from the composite MoGe target, but at varying distances from the Gd target. For each position, the deposition rate was calibrated by profile measurement of a test thick film; the thickness of films was controlled by the deposition time. Films within each series were fabricated in the same run under the same vacuum and deposition conditions. They have the same thickness but systematically varying Gd content.

Temperature dependence of sheet resistance for several representative Gd-doped films is shown as dashed lines in Fig. 1A. The magnetic doping simply shifts the superconducting transition, leaving its width and normal state resistance essentially unchanged. Figure 4 displays the critical temperature versus Gd content. Errors in the Gd content originate from uncertainty in the time of the deposition, deposition rate and positioning of a sample holder inside of the chamber. In addition, we found that thin A-type films with the same nominal thickness deposited in the same run revealed random variations in T_c. It is interesting to note that this effect was not detected in the B-type films deposited on Ge. In A-type films random deviations of T_c from the average value were always accompanied by the change in the normal state R_n of a film; in fact, there was no uncertainty in T_c vs R_n relation. The error in T_c resulting from this effect is indicated by vertical error bars in Fig. 4B. It was estimated from measurements on several series of undoped films deposited in the same conditions as the doped ones.

In Fig. 4B we showed with open circles the dependence of the T_c on Gd content for the thick MoGe films fabricated by three-gun (Mo,Ge and Gd) deposition in the extended range of doping. The dependence can be fitted by the Abrikosov-Gor’kov (AG) theory [26]. The critical concentration of Gd is 6.5 at. %; the corresponding volume critical concentration is n_c = 3 × 10^{21} cm^{-3}. 
The rest of the data were obtained with the two-gun deposition. The AG theory predicts that at low doping, $T_c$ behaves as $k_B(T_{c0} - T_c) = \pi \alpha/4$. The total pair-breaking strength, $\alpha$, is related to the pair-breaking strength per impurity as $\alpha = \alpha_p n_p$, where $n_p$ is the concentration of impurities. A linear suppression of $T_c$ is expected, and indeed was observed experimentally. The parameter $\alpha_p$ computed from the linear fit to the data, is plotted as a function of the film resistance in Fig. 5.

We found that with decreasing film thickness the pair-breaking strength in MoGe films deposited on Ge drops by about three times initially and saturates in films with thickness below 1.5 nm. From the fermionic theories we expect that $\alpha_p \approx \text{const}$; however this conclusion is made under assumption that the exchange coupling between a localized spin and conduction electrons doesn’t change with decreasing film thickness or increasing disorder.

The behavior of $\alpha_p$ in MoGe films appears to be qualitatively similar to the reduction of the Kondo contribution in thin films of normal metals doped with magnetic atoms [27]. Extensive studies of this effect revealed that it is stronger for impurities with integer spin [28] and depends on surface roughness [29]. The effect was explained in terms of spin-orbit induced magnetic anisotropy for magnetic impurities in proximity to the film surface [30]. The theory predicts that close to the surface the effective spin of a magnetic impurity is reduced.

Both the Kondo effect and magnetic pair-breaking depend on total impurity spin and exchange interaction between this spin and conduction electrons. From the known diffusion coefficient $D = 0.5 \text{ cm}^2/\text{s}$ [23] and spin-orbit scattering time $\tau_{so} = 5 \times 10^{-14} \text{s}$ [31] we can estimate the average spin-orbit scattering length in MoGe as $\ell_{so} = \sqrt{D \tau_{so}} \approx 1.6 \text{ nm}$. Experimentally, the $\ell_{so}$ coincides with the film thickness below which the saturation of $\alpha_p$ takes place. This observation suggests that the pair-breaking strength of a Gd atom is reduced when it is located within $\ell_{so}$ from the surface of a film; the growth of $\alpha_p$ in thicker films corresponds to the increasing fraction of Gd atoms with bulk-like surrounding. In other words, we have a gradual transition form anisotropic to isotropic exchange.

For all MoGe films deposited on Ge we found that the suppression of the superconductivity by the magnetic impurities and thickness reduction are additive processes. A magnetic impurity introduced into a superconductor suppresses the order parameter locally [32]. The local suppression of the order parameter with decreasing film thickness is also a feature of the fermionic mechanism of the SIT. In this regard, the additivity of the two processes even very close to the critical point of the SIT is consistent with the fermionic mechanism of the superconductivity suppression. Moreover, the $\alpha_p \approx \text{const}$ relation that we found in our thinnest films agrees with the specific prediction made within the fermionic model.

Let us now discuss how the magnetic doping affects thin A-type films. As shown in Fig. 4B, in the film with nominal thickness of 1 nm, the pair-breaking strength at low doping becomes zero; adding magnetic impurities to the film does not change its $T_c$. One possibility for this
anomalous response is that the spin-orbit induced magnetic anisotropy gets stronger in films deposited on SiN, because it has larger semiconductor gap. It is also possible that the anomalous response to the magnetic doping is related to the enhanced roughness of the thin A-type films, which may result in inhomogeneous superconducting state. Spacial non-uniformity of the order parameter is a common ingredient of the bosonic models. Analysis of the effect of magnetic impurities within these models can perhaps explain our findings.

In summary, we have studied the effect of magnetic doping on superconducting Mo$_{70}$Ge$_{30}$ films. For uniform films deposited on amorphous Ge, the suppression of superconductivity is consistent with the fermionic mechanism. In thin films deposited on SiN, the pair-breaking strength becomes zero. Further analysis is needed to explain this anomalous response.

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