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Mastering disorder in a first-order transition by ion irradiation

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The effect of ion-irradiation on MnAs single crystalline thin films is studied. The role of elastic collisions between ions and atoms of the material is singled out as the main process responsible for modifying the properties of the material. Thermal hysteresis suppression, and the loss of sharpness of the magneto-structural phase transition are studied as a function of different irradiation conditions. While the latter is shown to be associated with the ion-induced disorder at the scale of the transition correlation length, the former is related to the coupling between disorder and the large-scale elastic field associated with the phase coexistence pattern.

INTRODUCTION

The role of quenched disorder on phase changes has been addressed theoretically for several decades [1–5]. In the case of first-order transitions, unraveling the leading physical mechanisms responsible for the coupling between random impurities and order parameters is even a harder task. The coexistence of very different characteristic lengths and the presence of non-equilibrium features like hysteresis and kinetics make the task even more complex. Nonetheless, as most of the known large caloric effects take place on the verge of a first-order ferroic transition [6], mastering hysteresis and preserving other features (i.e. entropy and temperature changes) has been the focus of many investigations for the last two decades. At stake, beside the fundamental interest, such investigations can have a direct impact on the use of caloric effects for refrigeration and energy conversion applications [7–9]. Hysteresis reduction in magnetocaloric materials has been successfully achieved by acting on the phase transition globally, getting closer to a critical point through chemical change [10, 11], using a secondary external field [12–14], or using local non-homogeneity fostering phase nucleation. Indeed, controlling first-order phase changes in caloric materials using defects and disorder has been studied at different scales, from the atomic/chemical [15, 16], to the structural one [17, 18]. Thence, the possibility tuning the amount of disorder in a model system represents a unique opportunity for experimental investigations on phase change in solid-state systems. Moreover, it can pave the way developing new methods for tailoring the functional properties of materials where phase changes take place.

In this paper, we study the modifications induced by the collision and implantation of ions in manganese arsenide thin monocrystals. Bulk manganese arsenide (MnAs) shows a first-order magneto-structural transition from ferromagnetic to paramagnetic order accompanied by a lattice symmetry switch when getting above

the transition temperature $T_t = 313$ K [19]. From this perspective, MnAs can be considered as a prototypical first-order magnetocaloric material. Previous studies [20, 21] proved thermal hysteresis suppression in ion-irradiation MnAs films, keeping the caloric effect intensity unchanged. Here, the mechanisms underlying the modifications of the transition after ion-irradiation are investigated on single crystalline 150 nm thick MnAs films under different irradiation conditions (i.e. ion mass, ion kinetic energy, fluences, etc.).

EXPERIMENTAL METHODS

Growth conditions

The MnAs films have been produced by molecular beam epitaxy on GaAs(001) 0.3 mm thick substrates with the α -MnAs[0001] axis parallel to GaAs[$\bar{1}10$] [22]. Due to the epitaxial strain, the phase coexistence between the ferromagnetic α -phase with hexagonal structure (NiAs-type) and the paramagnetic β -phase with orthorhombic structure, (MnP-type), takes place over an extended temperature range (280–320 K) [23], in contrast with the sharper transition observed at the temperature $T_t = 313$ K in bulk single crystals [24].

Irradiation conditions

Ion irradiation have been performed at two facilities: the electron-cyclotron ion source SIMPA facility (Paris, France) [25] At SIMPA, samples have been irradiated with different ions (helium, oxygen, neon, argon and krypton) with kinetic energies ranging from 22 to 260 keV. The ion fluence Φ has been varied between 1×10^{12} ions/cm² and 6×10^{15} ions/cm², corresponding to an irradiation time spanning, from few tens of seconds to several hours. The energy of the different ion beams and the incident angle have been chosen in order to reach

an average penetration depth corresponding to the half thickness of the film. At IRRSUD, a beam of isotopic ^{36}Ar with an energy of 35.28 MeV has been used. In this case, no ions are implanted in the MnAs film, with most of them being stopped in the GaAs substrate. The fluence has been varied from 4×10^{12} to 1×10^{15} ions/cm 2 .

During the interaction with a solid, the ion transfers its kinetic and potential energies to the target atoms by a series of processes that can be schematically separated into two categories: one due to the interaction with the target nuclei, and the other due to the interaction with the electrons. The electron interaction is inelastic, and entails small or no lattice distortion into the target. The ion energy losses, including those related to the potential energy of the ion, are transferred to the solid via excitation of phonons, with an increasing in temperature along the trajectory. Nuclear collisions are the most probable process at low velocity and/or for heavy ions [26–28]. Such collisions lead to the displacement of sample atoms from their site and, if the kinetic energy is sufficiently high, to a cascade of secondary collisions, with the creation of clusters of vacancies and interstitial atoms in the sample lattice [26]. For the same kinetic energy, heavy ions produce a higher number of collisions per ion than light ions. This is due to the higher cross-section of the primary impact and the more favorable momentum transfer to target atoms, as well as the consequent secondary collisions in the cascade.

At the ion kinetic energies of SIMPA (E_{kin} less than 300 keV), the main process responsible for induced modifications is the nucleus–nucleus interaction between incoming ions and sample atoms. At the ion kinetic energies of IRRSUD, the probability of nuclear processes decreases while inelastic processes start to occur. Due to the small ion potential energy ($E_p \lesssim 5$ keV), compared to the kinetic energy, and to the metallic nature of the MnAs samples, the local heating from the electron interaction is not expected to induce noticeable modifications in the material. Indeed, elastic nuclear collisions remain the leading process that modifies the properties of the irradiated sample.

RESULTS AND DISCUSSIONS

General considerations

The two main modifications observed after ion-irradiation are hysteresis reduction, and the loss of sharpness of the transition, often referred to as *rounding* [2] (see Fig.1). To investigate them, isofield thermomagnetic $M(T)$ curves have been measured at constant field $H = 1$ T by a SQUID device with H parallel to the in plane easy magnetization direction. This makes the proportionality between $M(T)$ and the ferromagnetic α -phase a reliable assumption even under the application of

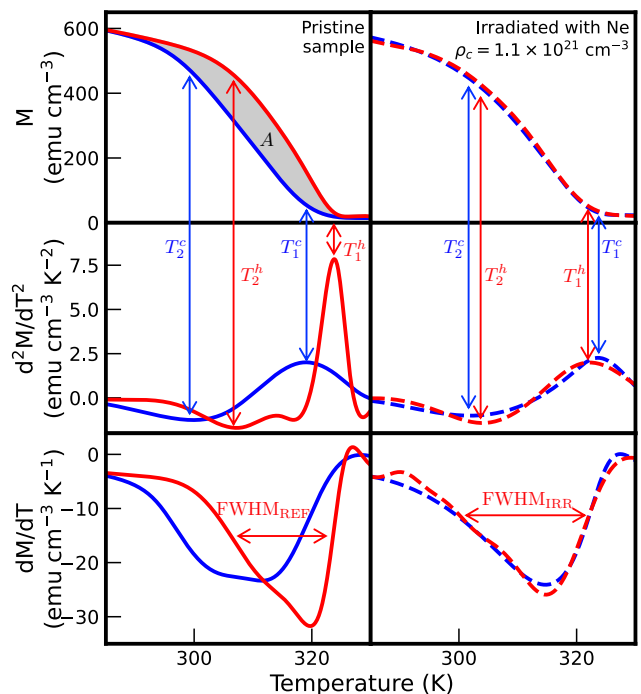


FIG. 1. Magnetization curves $M(T)$ (top) and corresponding first (bottom) and second derivative (middle) measured on reference (left) and irradiated (right) samples. Examples of FWHM_{REF} , and of FWHM_{IRR} , used in Eq.(1), are depicted in the bottom-left frame left and bottom-right, respectively. The temperatures T_1^h , and T_1^c corresponding to the maximum of the second derivative d^2M/dT^2 under heating, and cooling respectively are chosen to represent the upper limit of the phase coexistence interval. Similarly, T_2^h , and T_2^c , corresponding to the minima of the second derivative under heating, and cooling respectively, mark the lower bound of the same interval. The area A of the thermal hysteresis loop has been shaded in the upper frame. Cooling and heating curves are represented in blue and red, respectively.

a relatively small field of 1 T. Before each measurement, the material has been heated up to 350 K in order to erase any trace of the low-temperature phase, resetting the sample history [29]. Hysteresis, transition temperatures, and rounding are extracted from $M(T)$ curves and their derivatives. Whereas hysteresis, and its reduction, are phenomena taking place close to the transition temperature T_t , the transition rounding is associated with a widening of the phase coexistence region far away from it. Here, the thermal hysteresis width, ΔT_{hyst} , is evaluated from the area A between the $M(T)$ heating and cooling curves (Fig. 1 top) normalized to the saturation magnetization M_s measured at 100 K with $\Delta T_{\text{hyst}} = A/M_s$. This is an approach commonly used in the field of loss, and hysteresis modelling; it amounts to consider the effective width of an equivalent rectangular hysteresis cycle [30, 31]. Indeed, most samples have been irradiated within regimes where the maximum magnetization M_s is

not, or is marginally modified, as visible in Fig. 2.

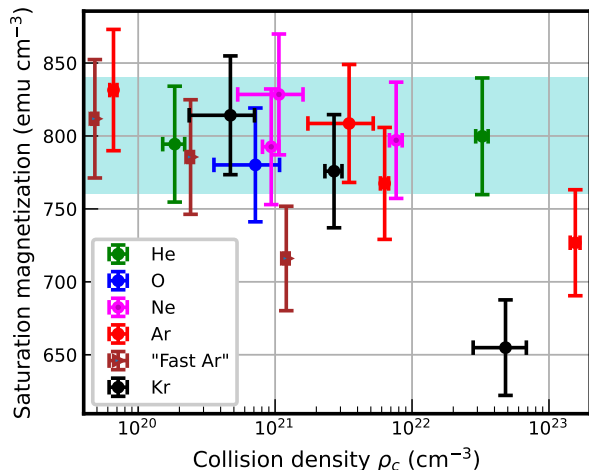


FIG. 2. Saturation magnetization (measured with $H = 1$ T at 100 K) as function of the collision density

Concerning the evaluation of the rounding, the data analysis has to disentangle the effect due to defects-induced disorder [13, 32] from the strain-induced broadening at the magnetostructural phase transition. The latter is characterized by a linear evolution of the phase fraction, across the transition, as a function of T . As shown in [22, 33–37], this behavior is driven by a mesoscopic phase-domain stripes pattern, and by its long-range elastic field. The former is relevant far from T_t and is associated with the presence of minority-phase regions whose stability is made possible by a local shift of T_t [2]. To tag the irradiation rounding effect only, we introduce the variable

$$\Delta T_{\text{rnd}} = \text{FWHM}_{\text{IRR}} - \text{FWHM}_{\text{REF}} \quad (1)$$

obtained by the width at half maximum (FWHM_{IRR}) of the first derivative of $M(T)$ of the irradiated films minus the contribution FWHM_{REF} of the pristine sample (see Fig. 1 bottom). The second derivative d^2M/dT^2 is used to identify the main part of the phase coexistence interval bounded by the maximum (at the temperature T_1) and the minimum (at T_2) of d^2M/dT^2 respectively. Some typical irradiation-induced modifications are presented, as an example, in Fig. 1 where the extrema of d^2M/dT^2 under heating (T_1^h , and T_2^h), and cooling (T_1^c , and T_2^c) are marked over the $M(T)$ of the pristine, and of an irradiated sample.

Hysteresis: Implanted ions vs induced collisions

In order to disentangle the role of binary-collisions-induced defects, from the one of ion implantation in

modifying the target properties, we first compare sample features with respect to the average collision density or the implanted ion density, ρ_c , and ρ_i , respectively. These quantities are estimated using the applied ion fluences, and the output of the ion-matter interaction Monte Carlo code SRIM/TRIM [38, 39]. More precisely, the outputs from the *Detailed Calculation with Full Damage Cascades* mode are considered, which include the position and number of the produced defects. ρ_c is obtained from vacancies and interstitial defects. The two densities induced by irradiating a sample of thickness t with a fluence Φ are estimated through the following expressions: $\rho_i = f\Phi/t$, and $\rho_c = N_{\text{coll}}\Phi/t$, where f , is the fraction of ions stopped, and N_{coll} is the average number of binary collisions induced by a single ion in the film. Despite the well-known SRIM/TRIM trend of slightly overestimating the number of induced defects [26, 28, 40], the predicted agglomerations (i.e. mixed-up vacancies and interstitials clusters) are rather similar to the ones obtained by advanced many-body molecular dynamics calculations taking into account collective behavior and temperature effects [27, 28, 41–43], and to the ones observed experimentally as well [44]. For our specific cases, f , and N_{coll} have a range of [0, 1] and [50, 5000], respectively. Thus, ρ_i and ρ_c differ by orders of magnitude and strongly depend on the projectile ion characteristics.

In Fig.3 we can see that, whereas no correlation is apparent between ΔT_{hyst} and ρ_i , a clear trend can be appreciated when ΔT_{hyst} is plotted against ρ_c . More precisely, ΔT_{hyst} decreases as a function of ρ_c until its total suppression at $\rho_c \approx 10^{21} - 10^{22} \text{ cm}^{-3}$. It is noteworthy that the three points relative to fast Ar irradiation, where no ions get implanted into the sample, spread over the same hysteresis decreasing trend curve when plotted against ρ_c . This is one of the main findings of this study, and it shows that the relevant defects are the ones produced by binary elastic collisions.

Hysteresis: additional insights

To get a better insight into the mechanisms underlying thermal hysteresis in MnAs films, the amplitude of the phase coexistence interval is studied over heating, and cooling as a function of ρ_c . When hysteresis is present, the aforementioned second derivative maximum and minimum show different values along the cooling and heating curves (see Fig. 4).

More precisely, the upper limit of the phase coexistence interval under heating, T_1^h , and cooling T_1^c are rather similar, and their difference $\Delta T_1 = T_1^h - T_1^c$, shown in Fig. 5 (bottom), stays close to zero in all samples, and does not show any specific trend as a function of the collision density ρ_c . On the contrary, the difference $\Delta T_2 = T_2^h - T_2^c$ between T_2 over heating, and cooling shown in Fig. 5 (top) is relevant in the pristine sample and gets reduced,

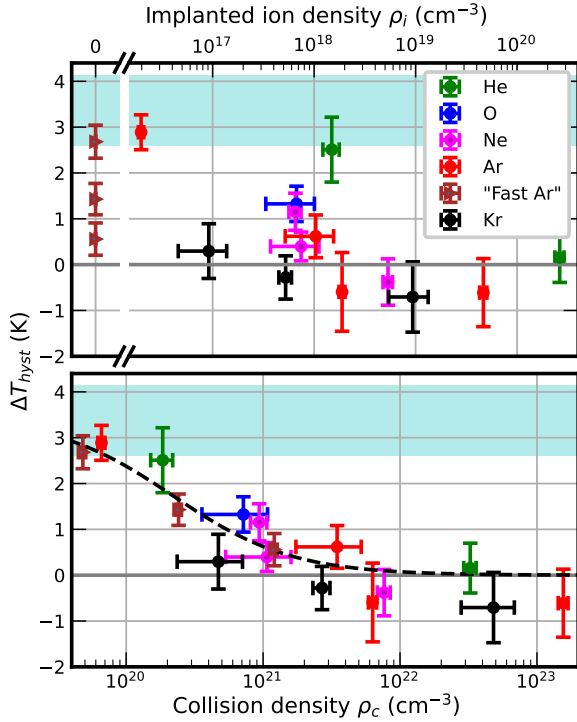


FIG. 3. Thermal hysteresis area as a function of the average density of implanted ions ρ_i (top), and of the average density of elastic collisions ρ_c (bottom). In light blue, the value of the pristine sample is reported. The uncertainties on the x -axis are mainly determined by the fluence evaluation, which can be critical for some beam preparation. The uncertainty on the y -axis is due to the SQUID measurement and the interpolation of the data affected by noise. The dashed line represents the best fit of the data with the formula discussed in the text.

and eventually suppressed, as a function of ρ_c following a trend similar to the one of ΔT_{hyst} . In Fig. 4 the values of T_2^h , and T_2^c are marked with dashed lines (red and blue, respectively), over the $M(T)$ curves of different samples. In the same figure, a single black dashed line marks T_1 over the reference and the irradiated samples. Following [34], T_1 can be considered the closest approximation to the actual transition point T_t (i.e. the one of a bulk single crystal). On the other hand, as apparent from Fig. 4, the reduction of hysteresis takes place as an increasing of T_2^c , in irradiated samples, with no change of T_2^h . In other words, hysteresis disappears through the collapse of the cooling $M(T)$ curve onto the heating one. Thence, hysteresis is mainly associated with supercooled metastable states.

Hysteresis is suppressed by ion-irradiation within the collision density interval $3 \times 10^{20} \text{ cm}^{-3} \lesssim \rho_c \lesssim 10^{21} \text{ cm}^{-3}$ (see Fig. 4). However, as clearly put in [34], after the first nucleation stage, the phase-coexistence stripes pattern builds up and the resulting thermal hysteresis can hardly be explained through a droplet-nucleation mech-

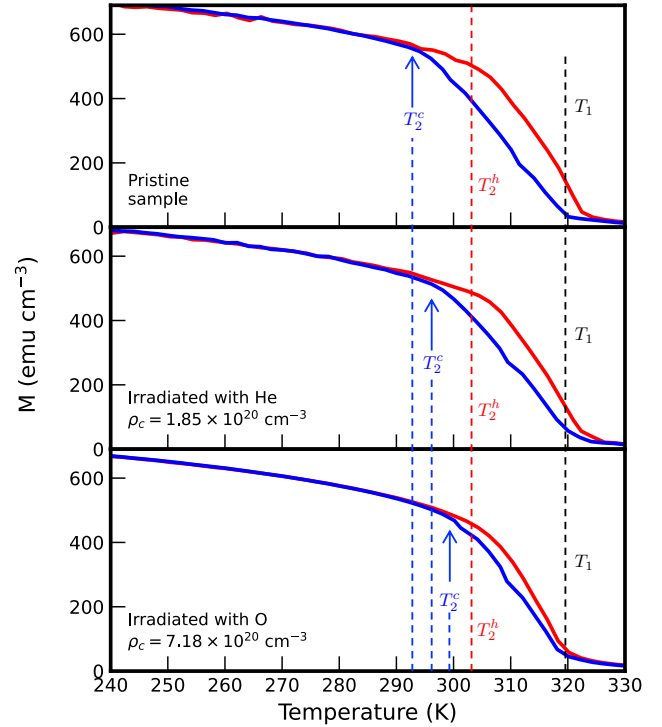


FIG. 4. Comparison between $M(T)$ loops over heating, and cooling (in red and blue), measured on the pristine sample (top), on a He irradiated sample (middle) and on an O irradiated sample (bottom). As apparent from Fig. 5, ΔT_1 is rather small and does not show any clear trend as a function of the collision density. Thence, a single dashed black line is used to mark T_1 over all the curves. On the contrary, ΔT_2 reduces as a function of ρ_c . Furthermore, this reduction takes place at fixed T_2^h (i.e. the single dashed red line), with T_2^c getting higher and closer to T_2^h as a function of the collision density (i.e. as shown by the sequence of blue dashed lines in the three frames of the figure).

anism. While only the cooling dM/dT curve plotted in Fig. 1 (bottom) for the non-irradiated sample shows a good agreement with the linear phase-evolution picture described in Refs. [33, 34], all the other curves show a non-linear $M(T)$. Besides, Fig. 1 (bottom) and Fig. 6 show that the hysteresis reduces jointly with the loss of linearity of the cooling $M(T)$ curve with higher values of the maximum of dM/dT implying faster phase kinetics. Similar asymmetries are a rather common feature of first-order phase transitions, from the best-known example of the water-ice transition to the different kinetics observed under cooling, and heating in FeRh films [45]. Here, as noticeable in Fig. 4, the difference between the cooling, and heating $M(T)$ curves depends on the lower slope of the formers, and on the entailed lower T_2 (i.e. a coexistence region lasting till a lower temperature). The loss of linearity and the increasing slope, going hand-in-hand with the hysteresis reduction, take place where the kinetics is led by the stripes domain elastic field. Therefore,

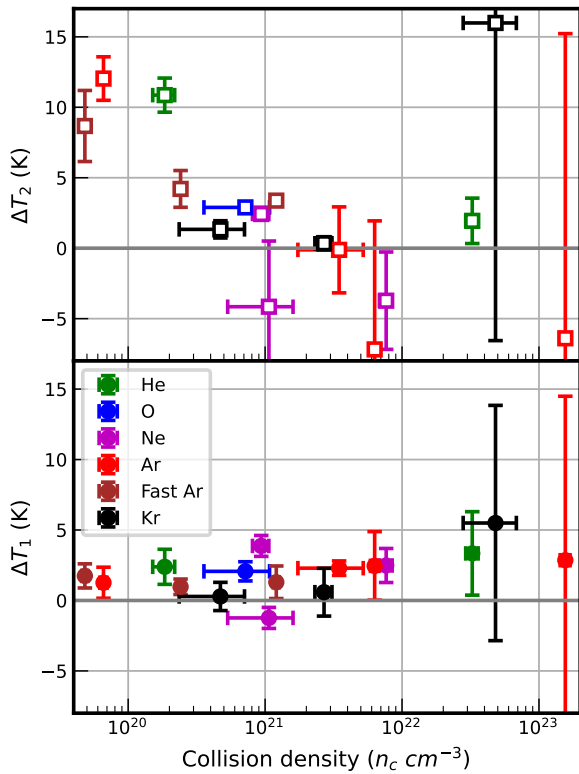


FIG. 5. Differences $\Delta T_2 = T_2^h - T_2^c$ (top), and $T_1 = T_1^h - T_1^c$ (bottom) between the extrema of the coexistence interval over heating and cooling as function of ρ_c . $\Delta T_2 = T_2^h - T_2^c$ reduces as a function of ρ_c , similarly to ΔT_{hyst} . ΔT_1 instead is, on average, close to 0, and does not show any specific trend as a function of ρ_c .

all these modifications can be interpreted as a modification of the elastic field associated with the stripes domain structure.

A possible clue to explain this behavior comes from the observation of the distortion of the regular stripes pattern in MnAs films after ion irradiation [20], with an increasing density of finite-length stripes. These defects have been observed in non-irradiated samples too [22, 36, 37]. They are associated to the non-linear region of $M(T)$ and they mostly disappear within the ordered-stripes structure getting closer to the transition temperature. Finite-length stripes may behave as topological defects, modifying the elastic energy with their stress field, similarly to the way unbound edge-dislocations do in 3D solids [46, 47], and in 2D mesomorphic phases [48]. Their increased density in irradiated samples can be the origin of the suppression of the supercooled metastable states, either by changing the phase fraction through nucleation of pairs or by renormalizing the effective elastic constants.

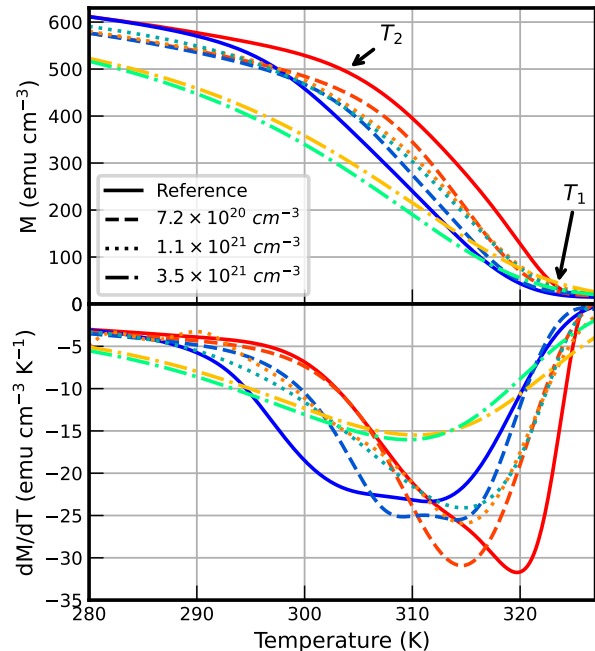


FIG. 6. Isofield ($H = 1$ T) magnetization curves $M(T)$ (top) and their first derivative (bottom) measured on reference (continuous lines) and irradiated (dashed lines) samples. Warm and cold colors correspond to heating and cooling curves, respectively.

This explanation, in spite of its being still rather conjectural, raises the question of the way ion-induced disorder directly modifies the phase-domain patterning where the relevant scale is the phase-domain characteristic length (i.e. the stripes spacing, $d_s \approx 0.73 \mu\text{m}$ [20]). Over such a large scale, the average collision density $\rho_c \propto p$ is expected to be the relevant quantity. The dashed curve in Fig. 3 (bottom) is obtained using as a fitting function

$$f(\rho_c) \propto \frac{1}{p_0 + p} = \frac{1}{p_0 + a \rho_c / \rho_0}, \quad (2)$$

where $\rho_0 = 2.92 \times 10^{22} \text{ cm}^{-3}$ is the atomic density of MnAs, a is a proportionality constant between p and ρ_c / ρ_0 that incorporates possible auto-healing processes, not taken into account by SRIM/TRIM, and possible activation thresholds, and p_0 is a constant describing the impurities present in the sample before the irradiation. When the value $a = 9.7\%$ from the rounding analysis (see next section) is considered, the value $p_0 = (7.3 \pm 2.3) \times 10^{-4}$ is found. It shows that, besides reducing hysteresis, collision-induced defects can be used to tailor the film domain pattern in the phase coexistence region.

Considering ρ_c as a figure of merit is equivalent to considering the total volume (V_{cas}) of the ion-induced collisional cascades like in Gibbons model [26, 49]. The collision density is, in fact, proportional to $n_c\phi/\Delta t$, where Δt is the thickness of the sample, ϕ is the ion fluence, and n_c is the number of collisions per ion, expected to be proportional to the single ion cascade $\langle V_{\text{cas}} \rangle$. Due to the relatively small value of ρ_c corresponding to the hysteresis disappearing, effects due to cascade overlaps can be excluded.

Rounding

The transition rounding ΔT_{rnd} , deduced from Eq.(1), also shows a systematic trend as a function of the collision density ρ_c (Fig. 7, top). Its departure from the reference value, at $\rho_c \approx 4 \times 10^{20} \text{ cm}^{-3}$, is followed by a strong increase with a slope depending on the ion type used for irradiation. Furthermore, the points collapse over the same curve when normalizing the relative rounding to the square root of the ion mass number m , $\Delta T_{\text{rnd}}/\sqrt{m}$ (Fig. 7, bottom).

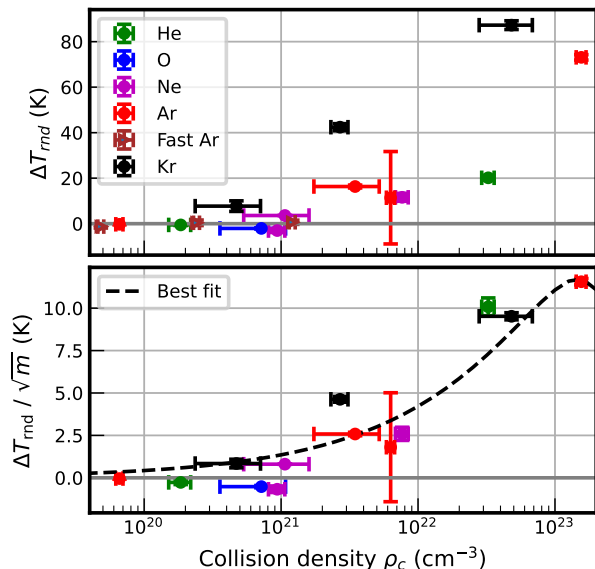


FIG. 7. Relative rounding ΔT_{rnd} from the FWHM of dM/dT curves without (top) and with \sqrt{m} mass rescaling (bottom). The dashed line represents the best fit of the data with the function $f(p) = c\sqrt{p(1-p)}$ (see text).

Differently from hysteresis suppression, which takes place near T_t where stripes domains and their long-range elastic field drive transition kinetics at the mesoscale [34], rounding takes place far from T_t where the only relevant scale is the phase transition correlation

length ξ . Indeed, the rounding behavior fits quite well within the approach reported in [2].

Considering a magnetic lattice model with a probability p to get a lattice site occupied by some sort of impurity, it is shown that, even when $p \ll 1$, a relevant transition rounding can appear due to the local fluctuations of impurity density. For a random impurity distribution, density fluctuations are proportional to the variance $p(1-p)$. The key issue to getting a stable rounding is the relationship between the phase transition correlation length ξ , and the characteristic size L of the regions where the impurity density fluctuation makes the minority phase energetically favored. Thence, the smearing-out of the transition is driven by the dimensionality d of the magnetic system, and by the way the interface energy between the two phases scales with respect to the region size L . Following [2], a spin lattice of dimensionality $d = 3$, with discrete symmetry, and with a surface tension between phases over a region of size L scaling as L^2 is expected to be unaffected by quenched disorder when $L < \xi$. Rounding appears when $L \sim \xi$, and scales as $\sqrt{p(1-p)}/L^3$ when $L > \xi$. Assuming the probability p , to get an impurity to be $p \propto \rho_c$, from Fig. 7 it can be deduced that $\xi \sim L$ when $\rho_c \approx 4 \times 10^{20} \text{ cm}^{-3}$. From cascade simulations, one can observe that one single ion forms several clusters of defects. The typical volume of collision clusters is $\propto 1/m$, where m is the ion mass. Assuming elastic-collision cascades as the origin of the impurities implies $L^3 \propto 1/m$, a feature that explains the higher slopes shown by samples irradiated with heavier ions and the collapse of all the points onto the same curve after the $1/\sqrt{m}$ normalization. Similar curves can be obtained by normalizing with respect to the number of collisions per ion and the average size of clusters of defects. Figure 7 (bottom) shows the mass normalized relative rounding data fitted with a function

$$f(\rho_c) = c\sqrt{a\frac{\rho_c}{\rho_0}\left(1 - a\frac{\rho_c}{\rho_0}\right)} \equiv c\sqrt{p(1-p)}. \quad (3)$$

From this analysis, a value of $a = (9.7 \pm 0.6)\%$ is found.

This shows that far away from the transition temperature, the minority phase develops as randomly distributed droplets before the building-up of the elastic-domain stripe structure as reported in [35, 37]. Whereas closer to T_t energy minimization is dominated by the long-range elastic interaction between stripes [33], in the first stages of the transition the leading energy terms are local, and fully led by the size L of regions where the precursor develops.

For the high-fluence regime considered for the rounding effect, one could also consider the effect of the collisional cascade overlapping. When we consider the simple model from Gibbons [26, 49], the fraction of the irradiated vol-

ume V_I over the total sample volume V_0 is given by

$$\frac{V_I}{V_0} = 1 - e^{-\frac{\langle V_{\text{cas}} \rangle \phi}{\Delta t}} = 1 - e^{-C\rho_c}, \quad (4)$$

with $\langle V_{\text{cas}} \rangle$ the average cascade volume, ϕ the ion fluence, and Δt the sample thickness. Introducing an appropriated constant C , this formula can be written in terms of collision density ρ_c (see previous section) and thus should be independent of the ion type. However, this approach does not consider the cascade fragmentation into defect clusters that is taken into account in our analysis by the \sqrt{m} dependence. Except for the very high density values of ρ_c , most of the data described here are expected to be in the regime with $p = \rho_c/\rho_0 \ll 1$, where cascade overlapping can be neglected.

CONCLUSIONS

In this work, we address the changes induced in MnAs thin films by ion irradiation. It is shown that elastic ion-atom collisions are the main mechanism responsible for modifying the magnetic properties of the material. Besides, modifications induced by ion collisions are shown to act at two different scales. In the short range, collisions serve as nucleation seeds of precursors responsible for the loss of sharpness of the phase change far from the transition temperature. At a larger scale, collisions modify the elastic energy by softening the long-range elastic field associated with the substrate coupling. Thus, new topological the creation of defects is favored in a distorted stripe pattern, and the thermal hysteresis is reduced until its elimination.

Disorder induced by light ions irradiation of magnetic thin films has been recently investigated through domain wall motion measurements focusing on spintronics applications [50]. Here, the effect of irradiation with ions of different mass is investigated through the behavior of the first-order magneto-structural transition on MnAs thin epitaxial films. Hysteresis suppression, transition rounding, and the tailoring of the phase-domain pattern are observed, opening unique opportunities in terms of applications to magnetocaloric devices, and to design of novel magnetic heterostructures.

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- [1] A. Brooks Harris, “Effect of random defects on the critical behaviour of Ising models,” *J. Phys. C: Solid State Phys.* **7**, 1671 (1974).
- [2] Yoseph Imry and Michael Wortis, “Influence of quenched impurities on first-order phase transitions,” *Phys. Rev. B* **19**, 3580 (1979).
- [3] James P Sethna, Karin Dahmen, Sivan Kartha, James A Krumhansl, Bruce W Roberts, and Joel D Shore, “Hysteresis and hierarchies: Dynamics of disorder-driven first-order phase transformations,” *Phys. Rev. Lett.* **70**, 3347 (1993).
- [4] A. Berger, A. Inomata, J.S. Jiang, J.E. Pearson, and SD Bader, “Experimental observation of disorder-driven hysteresis-loop criticality,” *Phys. Rev. Lett.* **85**, 4176 (2000).
- [5] T.R. Kirkpatrick and D. Belitz, “Stable phase separation and heterogeneity away from the coexistence curve,” *Phys. Rev. B* **93**, 144203 (2016).
- [6] X. Moya, S. Kar-Narayan, and N. D. Mathur, “Caloric materials near ferroic phase transitions,” *Nat. Mater.* **13**, 439–450 (2014).
- [7] O. Gutfleisch, T. Gottschall, M. Fries, D. Benke, I. Radulov, K. P. Skokov, H. Wende, M. Gruner, M. Acet, P. Entel, and M. Farle, “Mastering hysteresis in magnetocaloric materials,” *Phil. Trans. R. Soc. A* **374**, 20150308 (2016).
- [8] Julia Lyubina, “Magnetocaloric materials for energy efficient cooling,” *J. Phys. D* **50**, 053002 (2017).
- [9] Tino Gottschall, Konstantin P. Skokov, Maximilian Fries, Andreas Taubel, Iliya Radulov, Franziska Scheibel, Dimitri Benke, Stefan Riegg, and Oliver Gutfleisch, “Making a cool choice: The materials library of magnetic refrigeration,” *Adv. Energy Mater.* **9**, 1901322 (2019).
- [10] E. Brück, N.T. Trung, Z.Q. Ou, and K.H.J. Buschow, “Enhanced magnetocaloric effects and tunable thermal hysteresis in transition metal pnictides,” *Scr. Mater.* **67**, 590–593 (2012).
- [11] V. Franco, J. S. Blázquez, J. J. Ipus, J. Y. Law, L. M. Moreno-Ramírez, and A. Conde, “Magnetocaloric effect: From materials research to refrigeration devices,” *Prog. Mater. Sci.* **93**, 112–232 (2018).
- [12] Jian Liu, Tino Gottschall, Konstantin P. Skokov, James D. Moore, and Oliver Gutfleisch, “Giant magnetocaloric effect driven by structural transitions,” *Nat. Mater.* **11**, 620–626 (2012).
- [13] D. H. Mosca, F. Vidal, and V. H. Etgens, “Strain engineering of the magnetocaloric effect in MnAs epilayers,” *Phys. Rev. Lett.* **101**, 125503 (2008).
- [14] X. Moya, L. E. Hueso, F. Maccherozzi, A. I. Tovstolytkin, D. I. Podyalovskii, C. Ducati, L. C. Phillips, M. Ghidini, O. Hovorka, A. Berger, M. E. Vickers, E. Defay, S. S. Dhesi, and N. D. Mathur, “Giant and reversible extrinsic magnetocaloric effects in $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ films due to strain,” *Nat. Mater.* **12**, 52–58 (2013).
- [15] V. Sokolovskiy, V. Buchelnikov, M. Zagrebin, P. Entel, S. Sahoo, and M. Ogura, “First-principles investi-

- gation of chemical and structural disorder in magnetic $\text{Ni}_2\text{Mn}_{1+x}\text{Sn}_{1-x}$ heusler alloys,” *Phys. Rev. B* **86**, 134418 (2012).
- [16] A. Fujita, D. Matsunami, and H. Yako, “Realization of small intrinsic hysteresis with large magnetic entropy change in $\text{La}_{0.8}\text{Pr}_{0.2}(\text{Fe}_{0.88}\text{Si}_{0.10}\text{Al}_{0.02})_{13}$ by controlling itinerant-electron characteristics,” *Appl. Phys. Lett.* **104**, 122410 (2014).
- [17] Julia Lyubina, “Recent advances in the microstructure design of materials for near room temperature magnetic cooling,” *J. Appl. Phys.* **109**, 07A902 (2011).
- [18] R. Niemann, S. Hahn, A. Diestel, A. Backen, L. Schultz, K. Nielsch, M. F.-X. Wagner, and S. Fähler, “Reducing the nucleation barrier in magnetocaloric heusler alloys by nanoindentation,” *APL Mater.* **4**, 064101 (2016).
- [19] N. Menyuk, J.A. Kafalas, K. Dwight, and J.B. Goodenough, “Effects of pressure on the magnetic properties of MnAs,” *Phys. Rev.* **177**, 942 (1969).
- [20] M. Trassinelli, M. Marangolo, M. Eddrief, V. H. Etgens, V. Gafton, S. Hidki, E. Lacaze, E. Lamour, C. Prigent, J.-P. Rozet, S. Steydli, Y. Zheng, and D. Vernhet, “Suppression of the thermal hysteresis in magnetocaloric MnAs thin film by highly charged ion bombardment,” *Appl. Phys. Lett.* **104**, 081906 (2014).
- [21] M. Trassinelli, L. Bernard Carlsson, S. Cervera, M. Eddrief, V. H. Etgens, E. V. Gafton, E. Lacaze, E. Lamour, A. Lévy, S. Macé, C. Prigent, J. P. Rozet, S. Steydli, M. Marangolo, and D. Vernhet, “Low energy ne ion beam induced-modifications of magnetic properties in MnAs thin films,” *J. Phys. Condens. Matter* **29**, 055001 (2017).
- [22] R. Breitwieser, Franck Vidal, I.L. Graff, Massimiliano Marangolo, Mahmoud Eddrief, J.-C. Boulliard, and V.H Etgens, “Phase transition and surface morphology of MnAs/GaAs (001) studied with in situ variable-temperature scanning tunneling microscopy,” *Phys. Rev. B* **80**, 045403 (2009).
- [23] L. Däweritz, “Interplay of stress and magnetic properties in epitaxial MnAs films,” *Rep. Prog. Phys.* **69**, 2581 (2006).
- [24] R.H. Wilson and J.S. Kasper, “The crystal structure of mnas above 40 c,” *Acta Crystallogr.* **17**, 95–101 (1964).
- [25] A. Gumberidze, M. Trassinelli, N. Adrouche, C. I. Szabo, P. Indelicato, F. Haranger, J. M. Isac, E. Lamour, E. O. Le Bigot, J. Merot, C. Prigent, J. P. Rozet, and D. Vernhet, “Electronic temperatures, densities, and plasma X-ray emission of a 14.5 GHz electron-cyclotron resonance ion source,” *Rev. Sci. Instrum.* **81**, 033303–10 (2010).
- [26] M. Nastasi, J. Mayer, and J.K. Hirvonen, *Ion-Solid Interactions: Fundamentals and Applications* (Cambridge University Press, 1996).
- [27] Kai Nordlund, Steven J. Zinkle, Andrea E. Sand, Fredric Granberg, Robert S. Averback, Roger E. Stoller, Tomoaki Suzudo, Lorenzo Malerba, Florian Banhart, William J. Weber, Francois Willaime, Sergei L. Dudarev, and David Simeone, “Primary radiation damage: A review of current understanding and models,” *J. Nucl. Mater* **512**, 450–479 (2018).
- [28] K. Nordlund, “Historical review of computer simulation of radiation effects in materials,” *J. Nucl. Mater* **520**, 273–295 (2019).
- [29] Milan Bratko, Kelly Morrison, Ariana de Campos, Sergio Gama, Lesley F. Cohen, and Karl G. Sandeman, “History dependence of directly observed magnetocaloric effects in (Mn,Fe)As,” *Appl. Phys. Lett.* **100**, 252409 (2012).
- [30] Giorgio Bertotti, “Physical interpretation of eddy current losses in ferromagnetic materials. i. theoretical considerations,” *J. Appl. Phys.* **57**, 2110–2117 (1985).
- [31] Giorgio Bertotti, *Hysteresis in Magnetism: for Physicists, Materials Scientists, and Engineers* (Academic Press, 1998).
- [32] F. Vidal, O. Pluchery, N. Witkowski, V. Garcia, M. Marangolo, V. H. Etgens, and Y. Borensztein, “ $\alpha - \beta$ phase transition in MnAs/GaAs (001) thin films: An optical spectroscopic investigation,” *Phys. Rev. B* **74**, 115330 (2006).
- [33] V.M. Kaganer, B. Jenichen, F. Schippan, W. Braun, L. Däweritz, and K.H. Ploog, “Strain-mediated phase coexistence in heteroepitaxial films,” *Phys. Rev. Lett.* **85**, 341 (2000).
- [34] V.M. Kaganer, B. Jenichen, F. Schippan, W. Braun, L. Däweritz, and K.H. Ploog, “Strain-mediated phase coexistence in MnAs heteroepitaxial films on GaAs: An x-ray diffraction study,” *Phys. Rev. B* **66**, 045305 (2002).
- [35] T. Plake, M. Ramsteiner, V.M. Kaganer, B. Jenichen, M. Kästner, L. Däweritz, and K.H. Ploog, “Periodic elastic domains of coexisting phases in epitaxial MnAs films on GaAs,” *Appl. Phys. Lett.* **80**, 2523–2525 (2002).
- [36] T Plake, T. Hesjedal, J. Mohanty, M. Kästner, L. Däweritz, and K.H. Ploog, “Temperature-dependent magnetic force microscopy investigation of epitaxial MnAs films on GaAs (001),” *Appl. Phys. Lett.* **82**, 2308–2310 (2003).
- [37] L. Däweritz, M. Kästner, T. Hesjedal, T. Plake, B. Jenichen, and K.H. Ploog, “Structural and magnetic order in MnAs films grown by molecular beam epitaxy on GaAs for spin injection,” *Cryst. Growth* **251**, 297–302 (2003).
- [38] James F. Ziegler and Jochen P. Biersack, “The stopping and range of ions in matter,” in *Treatise on Heavy-Ion Science: Volume 6: Astrophysics, Chemistry, and Condensed Matter*, edited by D. Allan Bromley (Springer US, Boston, MA, 1985) pp. 93–129.
- [39] James F. Ziegler, M. D. Ziegler, and J. P. Biersack, “SRIM - the stopping and range of ions in matter (2010),” *Nucl. Instrum. Methods B* **268**, 1818–1823 (2010).
- [40] R. E. Stoller, M. B. Toloczko, G. S. Was, A. G. Certain, S. Dwaraknath, and F. A. Garner, “On the use of srim for computing radiation damage exposure,” *Nucl. Instrum. Methods B* **310**, 75–80 (2013).
- [41] K. Nordlund, J. Keinonen, M. Ghaly, and R. S. Averback, “Coherent displacement of atoms during ion irradiation,” *Nature* **398**, 49–51 (1999).
- [42] A. F. Calder, D. J. Bacon, A. V. Barashev, and Yu N. Osetsky, “On the origin of large interstitial clusters in displacement cascades,” *Philos. Mag.* **90**, 863–884 (2010).
- [43] Sang-Pil Kim, Huck Beng Chew, Eric Chason, Vivek B. Shenoy, and Kyung-Suk Kim, “Nanoscale mechanisms of surface stress and morphology evolution in fcc metals under noble-gas ion bombardments,” *Proc. R. Soc. A* **468**, 2550–2573 (2012).
- [44] Chenyang Lu, Ke Jin, Laurent K. Béland, Feifei Zhang, Taini Yang, Liang Qiao, Yanwen Zhang, Hongbin Bei, Hans M. Christen, Roger E. Stoller, and Lumin Wang, “Direct observation of defect range and evolution in ion-irradiated single crystalline Ni and Ni binary alloys,” *Sci. Rep.* **6**, 19994 (2016).
- [45] V. Uhlř, Jon Ander Arregi, and Eric E. Fuller-

- ton, “Colossal magnetic phase transition asymmetry in mesoscale ferh stripes,” *Nat. Commun.* **7** (2016).
- [46] Lev Davidovich Landau, Evgenij M Lifšic, Evgenii Mikhailovich Lifshitz, Arnold Markovich Kosevich, and Lev Petrovich Pitaevskii, *Theory of elasticity: volume 7*, Vol. 7 (pergamon, Oxford, 1986).
- [47] Frank Reginald Nunes Nabarro, “Mathematical theory of stationary dislocations,” *Adv. Phys.* **1**, 269–394 (1952).
- [48] Maurice Kleman and Oleg D. Lavrentovich, *Soft matter physics: an introduction* (Springer, 2003).
- [49] J. F. Gibbons, “Ion implantation in semiconductors—Part II: Damage production and annealing,” *Proc. IEEE* **60**, 1062–1096 (1972).
- [50] Johannes W. van der Jagt, Vincent Jeudy, André Thivaille, Mamour Sall, Nicolas Vernier, Liza Herrera Diez, Mohamed Belmeguenai, Yves Roussigné, Salim M Chérif, Mouad Fattouhi, *et al.*, “Revealing nanoscale disorder in W/Co-Fe-B/MgO ultrathin films using domain-wall motion,” *Phys. Rev. Appl.* **18**, 054072 (2022).