Nanoscale

PAPER

View Article Online
View Journal | View Issue

Cite this: *Nanoscale*, 2017, **9**, 13320

Magnetic exchange force microscopy: theoretical analysis of induced magnetization reversals†

Aleksei Ivanov,[a,b] Pavel F. Bessarab,[a,c] Valery M. Uzdin[b,c] and Hannes Jónsson *[a,d]

In magnetic exchange force microscopy a magnetic tip is scanned over the surface of a solid and an image representing the exchange interaction recorded. Sudden changes in the image corresponding to magnetization switching can be monitored as a function of the tip–surface distance thereby giving important information about the lifetime of metastable magnetic states and how it is affected by the exchange interaction. Here, theoretical calculations are carried out to study the tip–surface interaction and determine the mechanism and rate of transitions in a magnetic exchange force microscopy experiment, and comparison made with reported experimental data on an Fe cluster interacting with an antiferromagnetic Fe overlayer on a W(001) surface. The activation energy was determined from calculations of minimum energy paths and the pre-exponential factor in the Arrhenius rate expression evaluated from harmonic transition state theory, extended to account for zero modes. A noncollinear extension of the Alexander–Anderson model was used to describe the magnetic properties of an atomic scale representation of the system. The calculations reveal how the tip size, tip–surface distance and magnetic field affect the lifetime of the magnetic states.

Received 7th June 2017,
Accepted 4th August 2017

DOI: 10.1039/c7nr04036a

rsc.li/nanoscale

Magnetic states at a solid surface can be probed with atomic-scale resolution using an atomic force microscope equipped with a magnetic tip. One possibility is to probe the tip–surface interaction due to the long-range magnetostatic stray field. Another possibility is to base the imaging on the short-range exchange interaction in what is referred to as magnetic exchange force microscopy (MExFM).[1–4]

The magnetic exchange force between a tip and a surface, possibly including an adatom or adsorbed cluster on the surface, can also be used to manipulate magnetic states.[5–9] Since an electrical current does not flow between the tip and the surface in an MExFM experiment, the measurements are free from Joule heating and can be made on insulating samples.

Schmidt *et al.* have carried out extensive MExFM experiments on an antiferromagnetically ordered Fe monolayer on a W(001) substrate.[4,10] There, a Cr tip was intentionally brought into contact with the sample so that a magnetic Fe cluster became attached to the end of the tip. As the surface was scanned, the underlying atom on the surface alternated from having parallel (P) and antiparallel (A) ordering with respect to the Fe cluster at the tip. Occasionally, abrupt changes in the MExFM signal were observed indicating spontaneous magnetization switching in the cluster. Because of the limited laboratory time scale, transitions were observed only under specific conditions and for some of the prepared tips. The transitions occur on the time scale of the experiment from the less stable state, but the measurements cannot show whether this corresponds to P or A ordering of the magnetic moments of the cluster and the underlying surface atom. The MExFM experiment is illustrated schematically in Fig. 1. Two different values of a magnetic state lifetime could be determined at a temperature of 8.1 K, 17 ± 3 s and 27 ± 5 s, indicating an asymmetry in the energy of the cluster depending on the orientation of the magnetic moments. The number of atoms in the Fe cluster was estimated to be between 10 and 20.[10] This estimate is, however, uncertain because it relies on assumed values of several parameters, in particular the pre-exponential factor in the Arrhenius expression and the magnetic anisotropy.

Density functional theory (DFT) calculations within the generalized gradient approximation (GGA) have been carried out to study the interaction of small Fe and Fe/Cr tips with an antiferromagnetic Fe overlayer on W(001).[11,12] From the calculated energy difference between the two orientations of the magnetic moments of the tip as a function of distance, an absolute value could be assigned to the tip–surface distance in the experimental measurements. Calculations of the lifetime of magnetic states require, however, an evaluation of the acti-

---

[a] *Science Institute and Faculty of Physical Sciences, University of Iceland VR-III, 107 Reykjavík, Iceland. E-mail: hj@hi.is; Tel: +354 8923560*
[b] *Department of Physics, St. Petersburg State University, 199034, St. Petersburg, Russia*
[c] *Department of Natural Sciences, ITMO University, St. Petersburg, 197101, Russia*
[d] *Department of Applied Physics, Aalto University, Espoo, FI-00076, Finland*

† Electronic supplementary information (ESI) available. See DOI: 10.1039/C7NR04036A

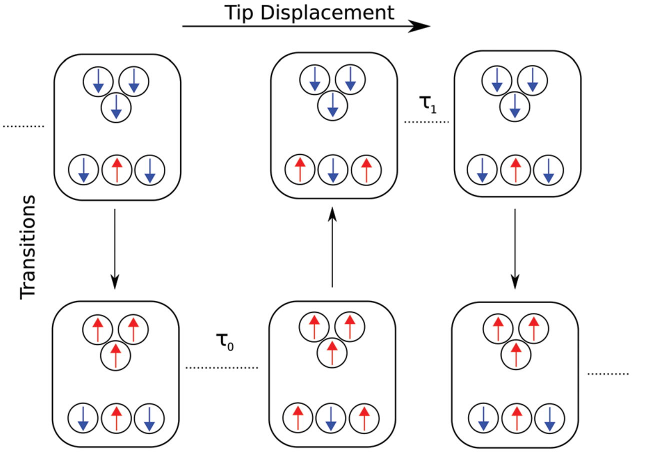

Fig. 1 An illustration of an MExFM experiment where the magnetic moments of a cluster at the tip can change orientation when the relative orientation with respect to the underlying surface atom is unfavorable. The favorable orientation is shown here to be parallel ordering of the tip and surface atom, consistent with the results presented here using a non-collinear extension of the Alexander–Anderson model. Due to a local magnetic field, the symmetry between the two orientations is broken and two slightly different values of the lifetime obtained, τ_0 and τ_1.

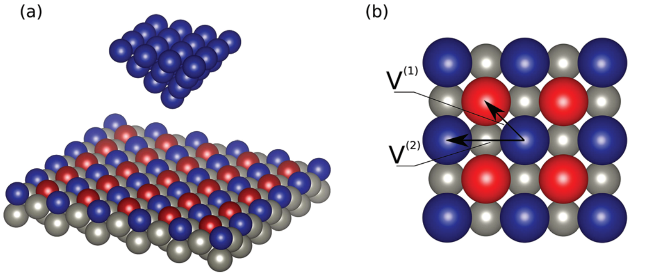

Fig. 2 (a) Illustration of the simulated system when the cluster at the tip is modeled as a four layer pyramid containing 30 Fe atoms. The atoms in the antiferromagnetic Fe overlayer are shown in blue/red to indicate parallel/antiparallel ordering of the magnetic moment with respect to the cluster at the tip. The underlying W atoms are shown in grey. The atoms at the boundary of the simulation cell are shown twice for clarity (but are equivalent because of periodic boundary conditions). (b) Since the distance between the atoms in the Fe overlayer is large, they interact through the conductivity band of the W substrate. The arrows indicate the interaction between first- and second-neighbor Fe atoms. There are twice as many Fe–W–Fe paths between first neighbors than second neighbors, so the hopping parameters in the NCAA models are chosen such that $V^{(2)} = V^{(1)}/\sqrt{2}$.

vation energy as well as the pre-exponential factor in the Arrhenius rate expression. Such calculations have not been reported previously for MExFM experiments.

In the present article, thermal stability of a magnetic cluster attached to a MExFM tip is evaluated using a non-collinear extension of the Alexander–Anderson model[13–16] and comparison is made with measurements.[10] Both the pre-exponential factor and the activation energy for the thermally activated transitions are evaluated as a function of tip–surface distance, cluster size and local magnetic field. An atomic scale model is constructed and found to give excellent agreement with the measured lifetimes.

The calculations were carried out for Fe clusters with the shape of a square pyramid interacting with a layer of Fe atoms commensurate with a W(001) surface. An example system is shown in Fig. 2 where the cluster contains 30 atoms, but calculations were carried out for clusters with 5 and up to 90 atoms. The surface was represented by a total of 50 Fe atoms subject to periodic boundary conditions in the plane of the surface. The non-collinear extension of the Alexander–Anderson model was used to evaluate the energy of the magnetic system.[13–16] This model has previously been used successfully to analyse, for example, remagnetization transitions of Fe clusters on the W(110) surface.[17] The energy of the d-band, E_0, and the on-site Coulomb interaction parameter, U, were chosen to have values in between those used to represent α-Fe[18,19] and Fe islands on W(110)[17] (those values differ only by a few percent, see ESI†). A parameter representing the interaction between d-electrons on different atoms ('hopping' parameter), and an anisotropy parameter for surface atoms, were chosen to reproduce results of DFT calculations and experimental measurements, in particular the variation of the exchange energy with distance (shown in Fig. 3)[10] and the calculated magnetic moment of surface overlayer atoms ($2.81\mu_B$ in NCAA, $2.67\mu_B$ from DFT[20]). An anisotropy axis pointing along the surface normal and an

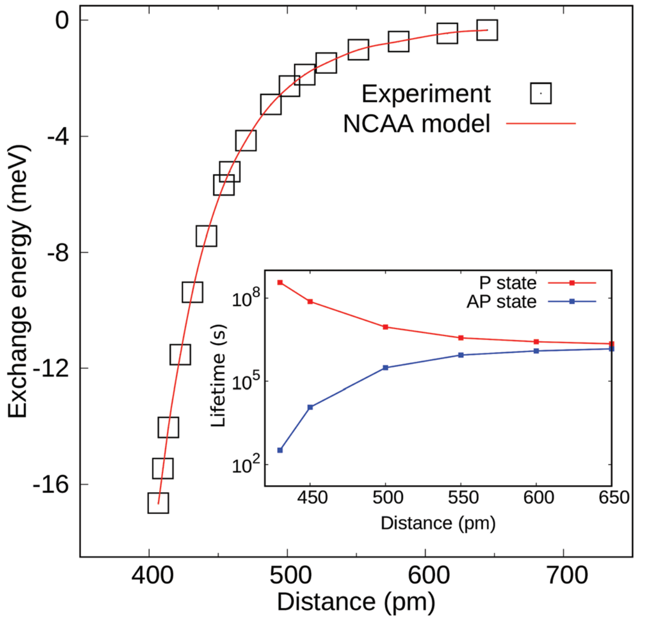

Fig. 3 (a) Exchange energy as a function of distance between Fe atoms at the end of the tip and in the overlayer. Open squares show values deduced from the MExFM measurements.[10] They were used here to determine the hopping parameter in the NCAA model for the interaction of the cluster with the surface. Solid line shows calculations performed for a 30 atom cluster, but the exchange energy is not sensitive to the cluster size. Inset: Calculated lifetime of the two magnetic states of the cluster, parallel and antiparallel ordering with respect to the underlying surface atom, as a function of distance.

anisotropy constant of 1.0 meV per atom for the tip cluster was used as was done by Schmidt *et al.*[10] Clusters with 5 or more atoms were found to have ferromagnetic ordering with magnetic moment per atom ranging from $2.57\mu_B$ (at the sharp end of tip) to $3.08\mu_B$ (at the base of the pyramid). A more detailed discussion of the methodology is given in the ESI.†

The minimum energy paths (MEPs) for the magnetic transitions between P and A states were calculated using the geodesic nudged elastic band (GNEB) method.[21] The difference between the maximum energy along an MEP, a saddle point on the energy surface, and the initial state energy gives an estimate of the activation energy, E_a. The pre-exponential factor in the Arrhenius expression for the rate constant, turns out to be slightly temperature dependent in this case because of the presence of zero modes, *i.e.* degrees of freedom at the saddle point for which the energy does not change. The expression for the rate constant is (see ESI†) $k = \nu\sqrt{T}\exp(-E_a/k_BT)$ where ν is a temperature independent factor. The method for evaluating the pre-exponential factor is an extension of the harmonic transition state theory expression for magnetic systems.[22,23] The temperature dependence of the pre-exponential factor in the present case is connected with the existence of degrees of freedom at the transition state for which the energy does not change – so-called zero modes. The lifetime, τ, of the various magnetic states can be calculated once the pre-exponential factor and the activation energy have been determined, as an inverse of the rate constant, $\tau = 1/k$.

Results of minimum energy path calculations for a cluster containing 30 atoms are shown in Fig. 4. In the absence of a surface, the two magnetic states of the cluster have the same energy and the minimum energy path is symmetric. The energy barrier for transitions between the two states is calculated to be 32 meV. In the presence of the surface, both states are lowered in energy, but by a different amount. The energy of the state where the magnetic moments of the cluster atoms are pointing in the same direction as that of the underlying surface atom, the P states, is lowered more than the energy of the A state. The difference between the energy of the two represents the exchange interaction. The MExFM experiments were carried out under conditions where the exchange energy is 10 meV.[10] In the calculations this corresponds to a tip–surface distance of 4.3 Å where the P state has been lowered in energy by 33 meV, while the A state has been lowered by 23 meV (see Fig. 4). The energy barrier for transitions from the A state to the P state is then lower than for a free cluster, 25 meV, while the energy barrier for transitions from the P state to the A state is higher, 35 meV. As a result, the P states become more stable and only transitions from A to P states become relevant on the timescale of the experiment, as illustrated in Fig. 1. The calculations therefore indicate that the lifetime measured in the MExFM experiments corresponds to the lifetime of the A state.

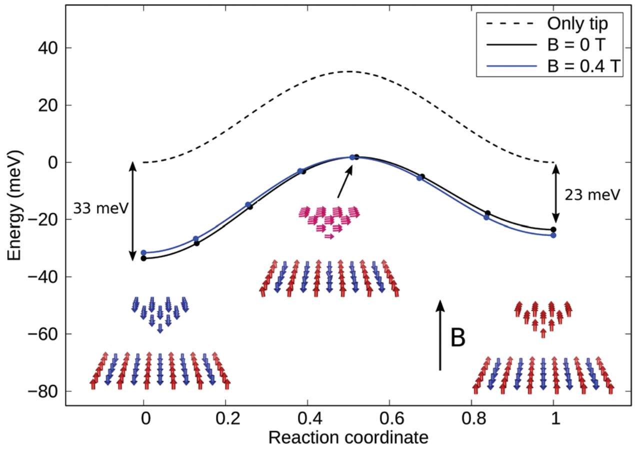

Fig. 4 The calculated minimum energy path for the reorientation of the magnetic moments of the cluster at the tip. Dashed line is for an isolated cluster in the absence of a surface. Solid black line is for a cluster with bottom atom 4.3 Å away from the surface where the exchange energy is 10 meV, as can be seen from the energy difference between the two orientations of the magnetic moments. Solid blue line shows the effect of a local field of 0.4 T in the direction of the surface normal. The reaction coordinate is the scaled total rotation of the magnetic moments along the minimum energy path. The insets show the magnetic vectors at the two energy minima and at the saddle point.

The fact that two different values of the lifetime were obtained in the MExFM experiments[10] indicates that the two A states are not of equal energy. This can be caused by a local magnetic field. The calculated results for the case where a quite large field of 0.4 T is pointing in the direction of the magnetic moments of the cluster in the A state are shown in Fig. 4. The activation energy for the transition to the P state is increased slightly since the energy of the maximum is unchanged. The lifetime of this A state becomes correspondingly longer. The other A state, where the magnetic moments of the cluster are pointing opposite to the local field becomes less stable and the energy barrier from that A state to the P state reduced, making its lifetime shorter.

The lifetime of the various magnetic states was calculated by evaluating the pre-exponential factor in the Arrhenius expression for the rate constant, as well as the activation energy obtained from the MEPs. For an isolated cluster in the absence of a surface, the results are shown in Fig. 5 and 6. The pre-exponential factor, $\nu\sqrt{T}$, is found to be large and a strongly increasing function of cluster size. For a cluster of 14 atoms at a temperature of 8 K, it is on the order of 10^{13} s^{-1} while for a 90 atom cluster it is 10^{18} s^{-1}. The activation energy is a nearly linear function of the number of atoms in the cluster. The calculated lifetime changes dramatically with the size of the cluster, as can be seen in the inset of Fig. 5. The lifetime of magnetic states in a cluster with *ca.* 20 atoms is predicted to be on the order of a second at a temperature of 8 K.

The effect of the interaction with the surface decreases the lifetime of the A states while the lifetime increases for the P states, as shown in Fig. 3 and 6. Now, a cluster with *ca.* 27 atoms has A states with a lifetime on the order of a second at a temperature of 8 K, while the lifetime of the P states is on the order of 10^6 s (11 days). The presence of a local magnetic field increases the lifetime of one of the A states (cluster-up/surface-down) and reduces the lifetime of the other (cluster-down/surface-

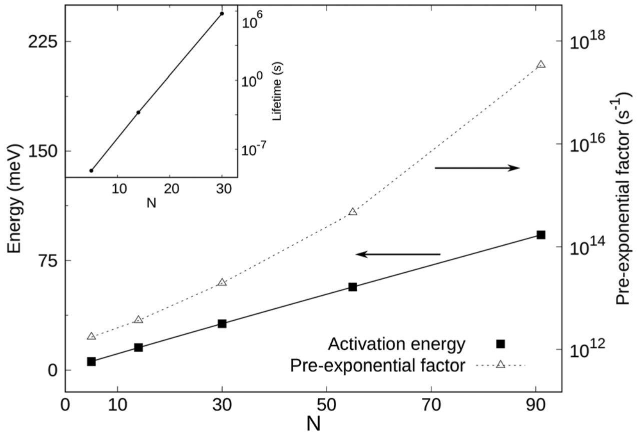

Fig. 5 The calculated activation energy (solid squares) and pre-exponential factor (open triangles) as a function of cluster size. Note the large, non-linear dependence of the pre-exponential factor on the size of the cluster. The calculations involve finding the minimum energy path for the transition to determine the activation energy and evaluation of the eigenvalues of the Hessian to determine the pre-exponential factor within harmonic transition state theory, extended to account for zero modes (see ESI†). Inset: Calculated lifetime of the magnetic state of an isolated pyramidal cluster as a function of cluster size, at a temperature of 8 K (no surface). The lifetime is a strong, exponential function of the cluster size.

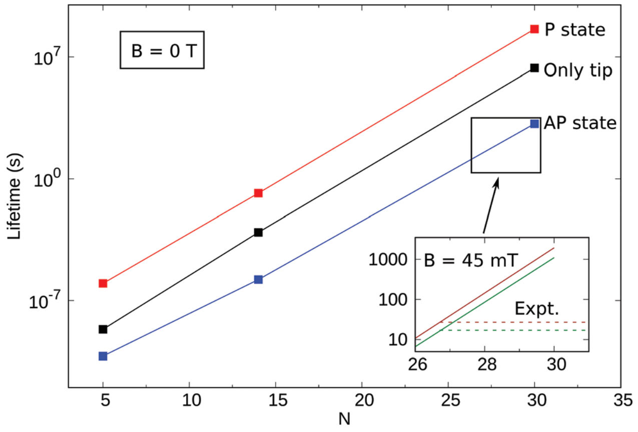

Fig. 6 Lifetime of magnetic states of the cluster at the tip evaluated for clusters of various size and a temperature of 8 K. Black line: Cluster in the absence of surface. Red line: State with parallel ordering with respect to the underlying surface atom at 4.3 Å from the surface. Red line: State with antiparallel ordering with respect to the underlying surface atom at 4.3 Å from the surface. Dashed lines show the two experimentally measured values of the lifetime.[10] Inset: Effect of a local magnetic field of 0.045 T pointing along the surface normal. This breaks the symmetry between the two antiparallel states (cluster-up/surface-down and cluster-down/surface-up) and gives two values of the lifetime in good agreement with the measured values.

up). For a local field of 0.045 T the calculated lifetimes are in close agreement with the lifetimes reported from the MExFM experiments,[10] 17 ± 3 s and 27 ± 5 s, as can be seen in Fig. 6.

The lifetime of the metastable states varies exponentially with the size of the Fe cluster at the tip, as illustrated in Fig. 5 and 6. A major challenge in a MExFM experiment carried out on a time scale of seconds at a fixed temperature is clearly the preparation of a tip with an appropriate number of magnetic atoms. At the low temperature of 8 K, the addition of just a few Fe atoms can change the lifetime of a magnetic state by orders of magnitude. Indeed, while many tips were prepared and tested in the MExFM experiments of Schmidt and co-workers, only a small fraction of them demonstrated thermal switching of magnetization on the timescale of seconds.[4,10] Variation of the tip–surface distance and, thereby, the magnitude of the exchange interaction also affects strongly the lifetime of the magnetic states, as illustrated in Fig. 3, and variation in the temperature of the system could also increase the range of useful cluster tips. Measurements over a range in temperature would also allow for direct measurements of the activation energy and pre-exponential factor for the magnetic transitions and provide valuable comparison with detailed, atomic scale calculations such as the ones presented here.

The calculated pre-exponential factor and the activation energy increase strongly with the size of the magnetic cluster. The large values obtained for the pre-exponential factor are noteworthy, but are in line with previous results obtained for Fe clusters adsorbed on a W(110) surface.[17] The increase with cluster size is likely due to the increasing number of low frequency vibrational modes at the saddle point configuration, leading to larger entropy of the transition state when many magnetic moments have been displaced during the transition. Similar effect has been seen in atomic rearrangements.[24] The increase in the activation energy with cluster size can be understood simply from the anisotropy, the barrier is essentially given by the number of atoms in the cluster times the anisotropy energy per atom, which is taken here to be 1.0 meV as has been done previously.[10] Further modeling of this system should include a careful estimation of the magnetic anisotropy of the magnetic cluster.

We obtain close agreement with the measured lifetimes of 17 ± 3 s and 27 ± 5 s with a magnetic cluster containing 27 atoms and local magnetic field of 0.045 T. This estimate of the cluster size is larger than the one given by Schmidt *et al.*, 10–20 atoms.[10] The main reason for this difference is the large value of the pre-exponential factor we obtain from the harmonic transition state theory calculations, 10^{13} s^{-1} at 8 K, as compared to the assumed value of 10^9 s^{-1}.[10]

The present calculations indicate that the observed transitions are from A arrangement of the magnetic moments of tip cluster and the underlying surface atom. The states with P arrangement are found to be lower in energy. This is opposite to the assignment deduced from DFT/GGA calculations.[12] The exchange interaction between the tip and the surface affects the stability of the magnetic states *via* two competing contributions of different origin.[14,25,26] In the A state, there is repulsion between the occupied d-band of one fragment (cluster or surface overlayer) and partly occupied d-band of the other fragment. Within second order perturbation theory, the change in energy due to this interaction is $\Delta E_A = -2\, V^2/U$.[14] Here, V is the hopping matrix element between d-states localized on different fragments and U is the on-site Coulomb integral for d-electrons. This contribution is referred to as kinetic exchange.[13,27] In the P state, hybridization of the occupied d-band of one fragment and the partially occupied d-band of the other fragment leads to the formation of bonding and anti-bonding spin orbitals and for sufficiently small interaction the energy lowering is $\Delta E_P = -V^2\rho_F$,[14] where ρ_F is the density of the d-band at the Fermi level. This is referred to as the double-exchange mechanism and is similar to the one introduced by Zener.[28] Both mechanisms, the kinetic exchange and the double-exchange mechanisms, are accounted for in the Alexander–Anderson model. A comparison of the energetics of the P and A states shows that the P state is favored if $U\rho_F > 2$. The preference of the DFT/GGA calculations for the A state may be due to the fact that U tends to be underestimated at that level of approximation because of the self-interaction error in the GGA functionals.[29,30]

Another difference between the present NCAA calculations and the DFT/GGA calculations is that the former assumes the system is in contact with a conducting metal (here the W substrate and the Cr tip) defining the Fermi energy, while the total number of electrons is fixed in the latter. A fixed Fermi level is a better representation of the experimental system since the tip and substrate are macroscopic and contain a large number of itinerant s(p)-electrons.

Schmidt *et al.* also reported experimental results of measurements taken in the presence of a large applied magnetic field of 4.5 T using a different tip.[10] Again, two lifetimes of metastable states were reported, 15 ± 4 s and 45 ± 17 s. This tip appears to have been quite different from the one used in the experiments discussed above because the overall magnetic moment must have been small, less than that of a single Fe atom. Possibly, the Fe cluster on the tip was much smaller in this case and the magnetic moments arranged in an antiferromagnetic or non-collinear way so as to give a small net magnetic moment. A smaller cluster can be influenced more strongly by the presence of the supporting antiferromagnetic Cr tip. In particular, the exchange interaction between the Fe cluster and the Cr tip can be affected by the presence of the applied magnetic field, possibly leading to an exchange bias effect.[31] The argument for such a small overall magnetic moment of the cluster in the high field experiment is as follows. Assuming the saddle point energy for the A → P transitions is hardly affected by an external field because the magnetic moments are roughly perpendicular to the field, the ratio of the two lifetimes gives the relative energy of the two A states as $\Delta E = k_BT\ln(\tau_1/\tau_2) = 0.7\ln 3\ \text{meV} = 0.8\ \text{meV}$. Assuming this energy difference is due to the Zeeman energy $\Delta E = 2MB$, the magnetic moment of the cluster, M, comes out to be $1.2\mu_B$. This is smaller than the magnetic moment of a single Fe atom, which ranges from $2.2\mu_B$ in α-Fe to $3.6\mu_B$ for an isolated Fe atom. Both NCAA and DFT calculations for small, ferromagnetic clusters of Fe give values of the magnetic moment per atom within this range. A realistic model of a cluster with a total magnetic moment of $1.2\mu_B$ is more challenging than the >20 atom cluster that is consistent with the zero field experiments. The modeling of such a small cluster would need to take the effect of the Cr tip explicitly into account, but that is outside the scope of the present study.

The calculations presented here assume the magnetic transitions take place by over-the-barrier transitions rather than quantum mechanical tunneling. The crossover temperature for tunneling in magnetic systems has been found to be on the order of 1 K or lower for molecular magnets[32] and up to 4 K for Fe islands on a surface.[33] While the onset temperature can be estimated from the energy landscape[34] we have not carried out such calculations here since the temperature in the experiments we compare our results with is significantly higher, 8 K.

In summary, we have calculated the lifetime of magnetic states in a MExFM tip using a detailed atomic scale model and compared the results with previously reported experimental data by Schmidt *et al.*[10] The NCAA model is used to describe the magnetic interactions and harmonic transition state theory used to estimate the lifetime of the magnetic states. Both the pre-exponential factor and the activation energy in the Arrhenius expression for the rate of the magnetic transitions are calculated for a wide range in the size of the magnetic cluster. The pre-exponential factor is found to be large, $10^{13}\ \text{s}^{-1}$, for the optimal cluster size of 27 atoms and a temperature of 8 K, and grow rapidly with the number of atoms in the cluster. The calculated lifetime of the two A states in the presence of a local field of 0.045 T is in close agreement with the values obtained experimentally[10] as shown in Fig. 6. This estimate, however, depends strongly on the value of the anisotropy parameter in the model and further analysis of this system should address this important issue, as well as the influence of the antiferromagnetic Cr tip on which the Fe cluster sits.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank Dr Alexander Schwarz, Dr Stefan Heinze and Dr Igor S. Lobanov for helpful discussions. This work was supported by the Academy of Finland (grant no. 278260), the Icelandic Research Fund (grants no. 163048-051 and 152483-052), the University of Iceland Research Fund, and the Mega-grant program of the Ministry of Education and Science of the Russian Federation (grant no. 14.Y26.31.0015).

References

1 U. Kaiser, A. Schwarz and R. Wiesendanger, *Nature*, 2007, **446**, 522.

2 R. Schmidt, C. Lazo, C. Hölscher, U. H. Pi, V. Caciuc, A. Schwarz, R. Wiesendanger and S. Heinze, *Nano Lett.*, 2009, **9**, 200.

3 R. Schmidt, C. Lazo, U. Kaiser, A. Schwarz, S. Heinze and R. Wiesendanger, *Phys. Rev. Lett.*, 2011, **106**, 257202.
4 R. Schmidt, A. Schwarz and R. Wiesendanger, *Appl. Phys. Lett.*, 2017, **110**, 061601.
5 A. J. Heinrich, J. A. Gupta, C. P. Lutz and D. M. Eigler, *Science*, 2004, **306**, 466.
6 K. Tao, V. S. Stepanyuk, W. Hergert, I. Rungger, S. Sanvito and P. Bruno, *Phys. Rev. Lett.*, 2009, **103**, 057202.
7 R. Wieser, V. Caciuc, C. Lazo, H. Hölscher, E. Y. Vedmedenko and R. Wiesendanger, *New J. Phys.*, 2013, **15**, 013011.
8 J. C. Oberg, M. R. Calvo, F. Delgado, M. Moro-Lagares, D. Serrate, D. Jacob, J. Fernandez-Rossier and C. F. Hirjibehedin, *Nat. Nanotechnol.*, 2015, **10**, 40.
9 S. Yan, D.-J. Choi, J. A. J. Burgess, S. Rolf-Pissarczyk and S. Loth, *Nat. Nanotechnol.*, 2015, **10**, 40.
10 R. Schmidt, A. Schwarz and R. Wiesendanger, *Phys. Rev. B: Condens. Matter*, 2012, **86**, 174402.
11 C. Lazo, V. Caciuc, H. Hölscher and S. Heinze, *Phys. Rev. B: Condens. Matter*, 2008, **78**, 214416.
12 C. Lazo and S. Heinze, *Phys. Rev. B: Condens. Matter*, 2011, **84**, 144428.
13 P. W. Anderson, *Phys. Rev.*, 1961, **124**, 41.
14 S. Alexander and P. W. Anderson, *Phys. Rev.*, 1964, **133**, A1594.
15 P. F. Bessarab, V. M. Uzdin and H. Jónsson, *Phys. Rev. B: Condens. Matter*, 2014, **89**, 214424.
16 P. F. Bessarab, A. Skorodumov, V. M. Uzdin and H. Jónsson, *Nanosyst.: Phys., Chem., Math.*, 2014, **5**, 757.
17 P. F. Bessarab, V. M. Uzdin and H. Jónsson, *Phys. Rev. Lett.*, 2013, **110**, 020604.
18 V. M. Uzdin, H. Zabel, A. Remhof and B. Hjörvarsson, *Phys. Rev. B: Condens. Matter*, 2009, **80**, 174418.
19 V. M. Uzdin, A. Vega, A. Khrenov, W. Keune, V. E. Kuncser, J. S. Jiang and S. D. Bader, *Phys. Rev. B: Condens. Matter*, 2012, **85**, 024409.
20 A. Kubetzka, P. Ferriani, M. Bode, S. Heinze, G. Bihlmayer, K. von Bergmann, O. Pietzsch, S. Blügel and R. Wiesendanger, *Phys. Rev. Lett.*, 2005, **94**, 087204.
21 P. F. Bessarab, V. M. Uzdin and H. Jónsson, *Comput. Phys. Commun.*, 2015, **196**, 335.
22 P. F. Bessarab, V. M. Uzdin and H. Jónsson, *Phys. Rev. B: Condens. Matter*, 2012, **85**, 184409.
23 P. F. Bessarab, V. M. Uzdin and H. Jónsson, *Z. Phys. Chem.*, 2013, **227**, 1543.
24 A. Pedersen and H. Jónsson, *Acta Mater.*, 2009, **57**, 4036.
25 A. Oswald, R. Zeller, P. J. Braspenning and P. H. Dederichs, *J. Phys. F: Met. Phys.*, 1985, **15**, 193–212.
26 P. Mavropoulos, S. Lounis and S. Blügel, *Phys. Status Solidi B*, 2010, **247**, 1187.
27 P. W. Anderson, *Solid State Phys.*, 1963, **14**, 99.
28 C. Zener, *Phys. Rev.*, 1953, **91**, 303.
29 J. P. Perdew and A. Zunger, *Phys. Rev. B: Condens. Matter*, 1981, **23**, 5048.
30 H. Jónsson, *Proc. Natl. Acad. Sci. U. S. A.*, 2011, **108**, 944.
31 R. L. Stamps, *J. Phys. D: Appl. Phys.*, 2000, **33**, R247.
32 W. Wernsdorfer, E. Bonet Orozco, K. Hasselbach, A. Benoit, D. Mailly, O. Kubo, H. Nakano and B. Barbara, *Phys. Rev. Lett.*, 1997, **79**, 4014.
33 S. Loth, S. Baumann, C. P. Lutz, D. M. Eigler and A. J. Heinrich, *Science*, 2012, **335**, 196.
34 S. Vlasov, P. F. Bessarab, V. M. Uzdin and H. Jónsson, *Faraday Discuss. R. Soc. Chem.*, 2016, **195**, 93.