Spin resonance amplitude and frequency of a single atom on a surface in a vector magnetic field

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We investigated spin-1/2 hydrogenated titanium (Ti) atoms on MgO using scanning tunneling microscopy (STM) combined with electron spin resonance (ESR) in vector magnetic fields. Rotating external magnetic fields, we observed rather drastic changes in both amplitude and frequency of resonance signals for single Ti atoms. While the variation of ESR amplitudes reflects the effects of the spin polarization of a magnetic tip and local magnetic fields created by the interaction between the tip and Ti, the change of resonance frequencies shows the anisotropy of g values for Ti atoms. Using the Ti atoms at the low-symmetry bridge adsorption site of the MgO lattice allowed for identifying the g values in all three spatial directions. Multiplet calculations confirmed the origin of this anisotropy as the spin-orbit coupling induced effects of crystal. Our results show the capability of single atomic spins as a sensor to probe magnetic surroundings and highlight the precision of ESR-STM to identify the single atom's spin states in a solid-state environment.

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I. INTRODUCTION

Single spins are widely regarded as an excellent candidate for realizing next-generation quantum devices for sensing [1–3] and information processing [4]. When placed in a solid-state environment, single spin centers, such as adatoms or point defects in a crystal, can be strongly influenced by their local environments of neighboring electron and nuclear spins [5,6], orbital and valley angular momenta [7–9], and static and fluctuating magnetic fields [10]. It is thus important to develop a technique that allows us to characterize the interactions between a spin center and its immediate surroundings.

Electron spin resonance (ESR) offers high energy resolution for the measurement of spins, which is not limited by the temperature. Scanning tunneling microscopy (STM), on the other hand, offers access to individual spins and to the surrounding environment at the atomic scale, albeit with an energy resolution that is limited by the temperature of tip and sample [11–13]. Recently, it was shown that these advantages could be combined in ESR-STM, which achieves an energy resolution of tens of neV with atomic-scale spatial resolution on individual spins [14,15].

In this paper, we positioned and probed a hydrogenated titanium (Ti) atom with spin 1/2 on MgO/Ag(100) using ESR-STM incorporated with a vector magnet. In such a setup, the atomic spin in the tunnel junction is subjected to a magnetic field provided by not only an external magnetic field but a spatially inhomogeneous magnetic field of tip. Two strengths of Ti on MgO make it desirable for study to identify the surface atom's magnetic surroundings which influence its spin state and thus its spin resonance. First, no zero-field splitting exists for spin 1/2 [16], and so the Ti spin follows the two-dimensional external magnetic field direction and acts as a rotatable sensor in the xz plane [Fig. 1(a)]. Second, the sizeable spin-orbit coupling of Ti makes it a sensitive probe to the substrate crystal field, the influence of which can be quantified by characterizing the g factor of Ti along the three principal axes. By rotating the single spin using the static external magnetic field, we are able to obtain a full spatial characterization of the tip magnetic field and the three-dimensional map of the surface spin's g factor from extensive ESR spectroscopic measurements.

II. METHOD

A. Experimental setup of single atom ESR measurement in low-temperature STM

We performed ESR measurements of single atoms on an ultraclean MgO surface using a home-built ultra-high-vacuum

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FIG. 1. The hydrogenated Ti atom on a bridge binding site (Ti_B) of MgO and corresponding ESR spectrum in a vector magnetic field. (a) Schematic of the ESR-STM setup combined with the spin density of Ti_B on MgO calculated by DFT. The external magnetic field rotates in a two-dimensional plane (xz plane) with the angle θ , which is measured relative to the sample surface normal (z direction). (b) STM images of Ti_B atoms with different binding configurations on MgO ($V_{\text{DC}} = 100$ mV, $I_{\text{set}} = 20$ pA (top) and 10 pA (bottom), and $T = 1.12$ K). The intercepts of grid lines represent the positions of oxygen atoms of the MgO lattice and were aligned using Ti and Fe atoms on top of oxygen as markers. Inset: The angle between the in-plane direction of the external magnetic field ($B_{\parallel}$) and a line connecting two neighboring oxygen atoms is φ . When $\varphi = 15.5^\circ$, Ti_B atoms are labeled as Ti_v . In the other case ($\varphi = 105.5^\circ$), they are labeled as Ti_h . Note that $\varphi = 105.5^\circ$ (Ti_h) is equivalent to $\varphi = 74.5^\circ$ due to the twofold symmetry. (c) ESR spectrum of Ti_v measured at $B_{\text{ext}} = 0.7$ T and $\theta = 90^\circ$ using tip 1 ($V_{\text{DC}} = 40$ mV, $I_{\text{set}} = 20$ pA, $V_{\text{RF}} = 10$ mV, and $T = 1.12$ K), and the solid line is the best fit to Eq. (1).

(UHV) scanning tunneling microscope with high-frequency transmission cables. The system can reach a base temperature of 30 mK using a dilution refrigerator system (Janis Research, JDR-250) when operated with ^3He - ^4He gas mixture. Throughout this paper, we measured ESR spectra at 1.12 K using only a small amount of mixture gas in the Joule-Thomson effect. The system is equipped with superconducting magnets which provide a vector magnetic field: maximum 9 T in the in-plane direction, 4 T in the out-of-plane direction, and 3 T when two magnets are simultaneously used.

Iron (Fe) and Ti atoms were subsequently deposited on two monolayers of MgO on Ag(100) at a temperature lower than 15 K. All adatoms on MgO can be easily identified by their apparent height in the STM images as well as by their unique spectral features in scanning tunneling spectroscopy (see Sec. S2 in the Supplemental Material [17]). As previously observed, Ti atoms exist in a hydrogenated state after absorbing residual hydrogen from the UHV chamber [16,18]. For simplicity we will refer to these hydrogenated Ti atoms as Ti

atoms from here on. The Ti atoms were found at two different binding sites: one on top of oxygen of the MgO lattice and the other at the bridge site between two oxygen atoms. In this paper, we measured ESR on the Ti atoms at the bridge binding sites (Ti_B) and used three different tips for the ESR measurements.

B. Calculations of the g -factor anisotropy

We performed magnetic multiplet calculations based on density functional theory (DFT) as previously reported in Ref. [19]. DFT calculations using pseudopotentials and plane-wave bases were performed in QUANTUM ESPRESSO (version 6.5) [20] with Perdew-Burke-Ernzerhof pseudopotentials from the standard solid-state pseudopotentials table (precision) [21] with a kinetic cutoff for the plane waves of 60 Ry and a dual of 10. The Brillouin-zone integration was performed on a $3 \times 3 \times 1$ Monkhorst-Pack k grid and dispersive forces were treated using Grimme's van der Waals correction [22].

Following previous reports, we modeled our system as two monolayers of MgO frozen at the lateral lattice constant of silver ($a_{\text{Ag,DFT}} = 4.16$ Å), expanded into a 1×1 nm² lateral supercell and padded by 15 Å of vacuum in the z direction [23]. A Ti atom was added to the cell above a bridge site between two oxygen atoms of MgO and the system was relaxed until all forces were less than 10^{-3} (Ry/ a_0). Then a hydrogen atom was added and the whole system was relaxed again. The relaxed structure was used to extract the coordinates and Lowdin charges were used as point charges in the multiplet calculations to represent the crystal field [24,25]. To accurately treat the Ti 3d manifold we are using scaled hydrogenic wave functions for spin-orbit coupling and electron-electron terms. The spin-orbit coupling strength was scaled to 90% of its value obtained from gas phase calculations ($\zeta = 18.948$ meV) [26], necessarily reduced due to the screening from the MgO substrate. The 3d-3d electron repulsion was scaled to 6.3 eV and the crystal field was strongly screened by 75%. The strong screening of the crystal field is most likely a consequence of significant on-site 3d-4s hybridization. Indeed, we find that the DFT wave function corresponding to the singly occupied $d_{x^2-y^2}$ state of Ti has about 10% contribution from the 4s orbital (see Sec. S5 in the Supplemental Material [17]).

III. RESULTS AND DISCUSSION

A. ESR spectra on Ti atoms with twofold symmetry

Ti atoms adsorbed at a bridge binding site of MgO can be seen by STM topography [Fig. 1(b)] and show two inequivalent binding sites with twofold symmetry. Their position can be easily changed by atom manipulation. The difference of two bridge binding sites originates from the relative angle of the MgO lattice with the external magnetic field and thus the Ti spin [27,28]. We label Ti at the two different bridge binding sites as vertical Ti_v and horizontal Ti_h . For Ti_v , the nearest neighbor oxygen atoms were almost aligned with the in-plane component of the external magnetic field, while they were almost perpendicular in the case of Ti_h [Fig. 1(b), inset]. By using these two inequivalent sites, we can determine the

FIG. 2. Anisotropy of the g factor of Ti_B . (a) ESR spectra of Ti_v (upper) and Ti_h (lower) at different angles θ of a vector magnetic field (same field magnitude) with tip 3 ($V_{DC} = 40$ mV, $V_{RF} = 10$ mV, $I_{set} = 20$ pA, $T = 1.12$ K, and $B_{ext} = 0.7$ T). (b) Current dependence of the resonance frequency of Ti_B measured with tip 2. Solid lines are fits considering the exchange interaction between STM tip and Ti_B . We give error bars with 95% confidence interval ($V_{DC} = 40$ mV, $V_{RF} = 10$ mV, $T = 1.12$ K, and $B_{ext} = 0.55$ T). (c) f_0 as a function of the angle θ . Each curve is fit to an ellipse in the xz plane, tracing along the shape of the two-dimensional anisotropic g factor. Error bars are from the fit in (b). (d) ESR frequency extrapolated to zero current (f_0) at different magnitudes of B_{ext} along the out-of-plane (left) and in-plane (right) directions. We obtained the g factors of Ti_v and Ti_h , $g_{v\parallel} = 1.679 \pm 0.003$ and $g_{h\parallel} = 1.901 \pm 0.020$ at the in-plane field direction, and $g_{v\perp} = 1.975 \pm 0.011$ and $g_{h\perp} = 1.991 \pm 0.019$ at the out-of-plane field direction ($V_{DC} = 40$ mV, $V_{RF} = 10$ mV, and $T = 1.12$ K). We note that the fit has a subtle offset near zero, which might come from a non-negligible dipole-dipole coupling on the extrapolated f_0 .

g factor along all three spatial directions by a series of ESR measurements.

An example of a typical ESR spectrum for Ti at the bridge binding site is shown in Fig. 1(c), measured by sweeping the frequency (f_{RF}) of a radio-frequency voltage (V_{RF}), at a constant external magnetic field B_{ext} . The ESR data were fitted to Eq. (1):

$$I = I_0 + \Delta I = I_0 + I_1 \frac{1 + \alpha \delta}{1 + \delta^2}, \quad (1)$$

where I_0 is the background current, ΔI is the ESR signal, δ is the normalized frequency ($\delta = \frac{f - f_{res}}{\Gamma/2}$) for the resonance frequency f_{res} and the linewidth Γ , I_1 is the amplitude of the current change of the ESR signal, and α is the asymmetry factor [18]. When α is zero, Eq. (1) corresponds to the Lorentzian function. From the fit shown in Fig. 1(c), we obtained a resonance frequency $f_{res} = 18.361 \pm 0.001$ GHz and the amplitude of the spectrum $I_1 = 835 \pm 11$ fA at $B_{ext} = 0.7$ T and tunnel current $I_{set} = 20$ pA.

B. Mapping the g -factor anisotropy of Ti atoms

To obtain a full three-dimensional map of the magnetic environment, we measured ESR spectra on Ti at two inequivalent bridge binding sites. Note that we define θ as the angle between the surface normal and the magnetic field direction. We vary the angle θ as well as the magnitude of the external magnetic field (B_{ext}) in a two-dimensional plane. Interestingly, we found a pronounced difference in the ESR spectra depending on the angle θ when measuring on Ti_v and Ti_h [Fig. 2(a)], while the resonance frequencies of both Ti_v and Ti_h increased and became more similar as we applied the magnetic field closer to the out-of-plane direction, indicating strong in-plane anisotropy. The observed shift of the ESR frequency of Ti_v with the angle θ of the magnetic field is almost three times larger than that of Ti_h [Fig. 2(a)].

The change of ESR frequency at different angles of B_{ext} results from the g -factor anisotropy of Ti atoms on MgO, which has also been found for Ti absorbed on the oxygen binding site [29]. In order to precisely determine the B_{ext} angle

FIG. 3. Three-dimensional map of anisotropic g factor and dynamic instability of a hydrogen atom on Ti. (a) Potential energy surface (PES) of a hydrogen atom on Ti/MgO. The Ti atom is located in the center of the figure with the x axis pointing towards O located at the red circles and the y axis towards Mg atoms (green). The insets show a line cut along x and y axis close to the center, clearly showing a pronounced double-well potential along the x direction. (b) Effective g factor plotted as functions of the in-plane angle (ϕ) and out-of-plane angle (θ) of $\mathbf{B}_{\text{ext}}$ as obtained from the multiplet calculations. The same values of the g factor are represented by contour lines. The values corresponding to Ti_v and Ti_h are indicated by vertical dashed lines, considering the symmetry of the MgO lattice.

dependence of the resonance frequency, it is necessary to eliminate the influence of the effective magnetic field created by a magnetic tip ($\mathbf{B}_{\text{tip}}$) by measuring the ESR spectra on Ti spin at different tip-Ti distances [30]. At a given $\mathbf{B}_{\text{ext}}$, the ESR frequency shifts with tip-atom separation d set by the tunnel current [Fig. 2(b)]. This shift is governed by two distinct terms of the tip field [16,31], the exchange field $B_{\text{exc}} \propto \exp(-d/d_{\text{ex}})$ and the dipolar field $B_{\text{dip}} \propto 1/d^3$. We found that the exchange field dominates for the tips used here, in line with several previous studies [18,32,33]. Extrapolating the resonance frequency f_0 at zero tunnel current allows us to determine the Zeeman energy depending only on the external magnetic field $\mathbf{B}_{\text{ext}}$.

The extrapolated resonance frequency f_0 is plotted as a function of the field angle θ in Fig. 2(c) at a constant magnitude of $B_{\text{ext}} = 0.55$ T. Near the out-of-plane direction ($\theta = 0^\circ$), Ti_v and Ti_h show the same ESR frequency. The resonance frequencies for Ti_v and Ti_h start deviating when rotating the field to the in-plane direction and eventually differ by about 1.54 GHz at the in-plane magnetic field ($\theta = 90^\circ$). Unlike Ti at an oxygen binding site on the same MgO surface [29], the different in-plane resonance frequencies of Ti_v and Ti_h reflect the lower twofold symmetry of the bridge binding site.

To determine the g factor along the three principal axes, we measured f_0 for both Ti_v and Ti_h as a function of magnetic field magnitudes B_{ext} at the magnetic field angles $\theta = 0^\circ$ and 90° [Fig. 2(d)]. From these measurements, the magnetic moments of the two Ti atoms were obtained from the linear fit of f_0 as a function of B_{ext} , which yields in-plane magnetic moments $\mu_{v\parallel} = (0.840 \pm 0.001)\mu_B$ and $\mu_{h\parallel} = (0.950 \pm 0.010)\mu_B$ for Ti_v and Ti_h , respectively. The out-of-plane magnetic moments for Ti_v and Ti_h are $\mu_{v\perp} = (0.987 \pm 0.006)\mu_B$ and $\mu_{h\perp} = (0.996 \pm 0.010)\mu_B$. Given

that in our sample the O-O bond direction (along the nearest neighbor oxygen atoms) of the MgO lattices was misaligned by 15.5° with the in-plane component of the external magnetic field [Fig. 1(b)], we were able to determine the g factors along the lattice directions: $g_{\text{O-O}} = 1.653 \pm 0.002$, $g_{\text{Mg-Mg}} = 1.917 \pm 0.019$, and $g_z = 1.989 \pm 0.024$. We confirmed that the result of an anisotropic g factor is reliable with several different tips and on other Ti atoms (see Sec. S6 in the Supplemental Material [17]).

C. Theoretical analysis of g -factor anisotropy

To unravel the origin of the g -factor anisotropy along different axes of the MgO lattice, we calculated the effective g factor along arbitrary directions of the external magnetic field $\mathbf{B}_{\text{ext}}$ [Fig. 3(b)] using a combination of DFT and magnetic multiplet calculations [34]. The hydrogenated Ti atoms in this system are known to have a dynamical instability of the hydrogen as the potential energy surface (PES) exhibits a double-well potential profile along the x axis, with minima pointing towards the oxygen atoms (see also Sec. S5 in the Supplemental Material [17]). We accounted for this instability in the multiplet calculations by sampling the PES of hydrogen in the presence of Ti and the MgO substrate [Fig. 3(a)]. We performed multiplet calculations to obtain the g factor under small displacements ($\Delta x, \Delta y$; see Table I) of the hydrogen atom relative to the Ti. The resulting g factor for each calculation was then weighted according to its statistical Boltzmann weight at $T = 1.1$ K with the energy obtained from the PES calculation [$E = f(\Delta x, \Delta y, \Delta z)$]. The calculated values for the g factor along the principal axes are in excellent agreement with the experiment as shown in Table II.

TABLE I. Point charge model used for the crystal field in the multiplet calculation. Shown are the (Lowdin) charges ($-|e|$) and Cartesian coordinates for each ion in the crystal field along the three different spatial directions, where Z is the out-of-plane direction and O-O and Mg-Mg represent the directions connecting each atom in the MgO lattice. All coordinates are relative to the Ti adatom.

Ion	Δ electrons (no.)	O-O (Å)	Mg-Mg (Å)	Z (Å)
O	+0.75	-1.36	0.0	-1.27
O	+0.75	1.38	0.0	-1.27
Mg	-0.73	0.0	-1.67	-2.10
Mg	-0.73	0.0	1.67	-2.10
H	+0.46	$0.00 \pm \Delta x$	$0.00 \pm \Delta y$	$1.76 \pm \Delta z$

The multiplet calculations also reveal the origin of the anisotropy to lie in a gradual reduction of the orbital moment which is coupled antiparallel to the spin when rotating the external magnetic field direction from the in-plane to the out-of-plane direction. The magnitude of the reduction depends on the azimuthal angle as shown in Fig. 4, which indicates the contribution of the orbital moment is less than about $0.1 \mu_B$ in the plane ($\theta = 90^\circ$). This presence of orbital momentum strongly affects the total momentum through the spin-orbit coupling, causing the anisotropy of the g factor.

D. ESR amplitude analysis and the model fit

We will now focus on the change of amplitudes of ESR signals when rotating the external magnetic field. Knowing the intrinsic properties of the Ti spin on MgO, we can use it as a probe to investigate how the magnetic interaction with the tip influences the ESR signals, which might hint why the spin polarization of the tip does not guarantee measurement of ESR signals. Note that measured Ti atoms are well isolated from other atoms on the surface (Supplemental Material [17]) but the tip spin is positioned on top. Two examples of ESR spectra for Ti measured with different tips as a function of the magnetic field direction θ are given in Figs. 2(a) and 5(a), which show rather dramatic changes of the amplitude of the ESR signals as a function of θ . This variation is a consequence of the different relative alignment between the Ti spin and the unknown spin of the magnetic cluster at the tip. Considering the piezoelectric coupling (PEC) model for a single atom ESR in STM, the spin at the tip plays two important roles: (i) providing an oscillating magnetic field to drive the ESR transitions [33,35] and (ii) detecting the ESR signals based on the tunneling magnetoresistance effect [18,36].

In the PEC model, the Ti atoms experience a time-varying magnetic field under the spatially inhomogeneous effective

TABLE II. Values for the g factor obtained from experiment and multiplet calculations.

g -factor element	Experiment	Multiplet
g_{O-O}	1.653 ± 0.002	1.67
g_{Mg-Mg}	1.917 ± 0.019	1.91
g_z	1.989 ± 0.024	1.99

FIG. 4. Thermal averages at 1.1 K for the expectation value of spin and orbital moment along the external magnetic field direction for two azimuthal values $\varphi = 15.5^\circ$ (Ti_v) (a) and $\varphi = 74.5^\circ$ (Ti_h) (b) for changing θ measured from the out-of-plane direction. The anisotropy of the g factor is the result of the antiparallel coupling of orbital and spin moment.

magnetic field, B_{tip} , as a consequence of the adiabatic coupling of the motion of the Ti to the rf voltage [32,35]. To explain our data, we assume that the tip spin has a strong easy-axis magnetic anisotropy, which keeps the tip spin aligned in a certain direction fixed in the laboratory frame while B_{ext} changes. However, we have to consider that the tip spin can flip by 180° to minimize its Zeeman energy (i.e., it is pointing up or down along its easy axis), which is indicated by the 180° periodicity of the signal [Fig. 5(b)]. Figure 5(c) introduces the coordinates used in the model. The xyz coordinates are determined by the surface normal (z) and the plane of B_{ext} (xz plane) as defined in Fig. 1(a), whereas the $x'y'z'$ coordinate is defined to have the z' axis along the quantization axis of the Ti spin fixed by the direction of the external magnetic field. Note that we assume $B_{ext} + B_{tip} \approx B_{ext}$ for ESR amplitude analysis.

The simplified equation for the ESR amplitude I_1 based on the PEC model is given by

$$I_1 \propto \Phi(\Omega)[\langle S_{tip} \rangle \cdot \langle S_{Ti} \rangle], \quad (2)$$

where Ω is the Rabi rate and $\Phi(\Omega) = \Omega^2 T_1 T_2 / (1 + \Omega^2 T_1 T_2)$ is the driving factor on resonance, which ranges from 0 to 1 depending on how far the spin population is driven into equal state population [37,38]. Equation (2) shows that the ESR signals are determined by the product of the driving strength ($\Phi(\Omega)$) and the spin contrast for the detection ($\langle S_{tip} \rangle \cdot \langle S_{Ti} \rangle$). The detailed fit function is described in Secs. S7 and S8 in the Supplemental Material [17].

As hinted in Eq. (2), rotating the magnetic field impacts driving and detection simultaneously. The influence on driving the ESR transition can be understood by assuming the quantization axis of the Ti spin S_{Ti} along the z' direction; the x' and y' components of B_{tip} provide the driving magnetic field B_1 of ESR transitions, where we choose $y' = y$. Since the Ti spin is aligned along the external magnetic field, rotating this field in the xz plane results in a corresponding exchange of the amplitudes of the x' and z' components of B_{tip} as

FIG. 5. ESR amplitudes at different directions of magnetic fields for Ti_h as a probe of the tip magnetic field. (a) ESR spectra at different angles (θ) of the external magnetic field using tip 1 ($V_{\text{DC}} = 40$ mV, $I = 20$ pA, $V_{\text{RF}} = 10$ mV, $T = 1.12$ K, and $B_{\text{ext}} = 0.7$ T). (b) ESR amplitude as a function of the magnetic field angle, θ . The ESR amplitude of each point is extracted from the fit of ESR curves in (a) to Eq. (1). The solid line is a fit to the model described in the main text and Secs. S7 and S8 in the Supplemental Material [17]. (c) Schematic of the relative spin orientations of tip (left) and sample (right). We define the x and z axis as in-plane and out-of-plane directions of the sample surface, respectively, as defined in Fig. 1(a). The direction of the tip spin is denoted by the angles γ and χ with respect to the y and z axes in the laboratory frame. At the right, the rotated coordinate system, where the z' axis is the quantization axis of the Ti spin, is given to have the $x'z'$ plane lie on the xz plane in the laboratory frame since we rotate B_{ext} in that plane ($y' = y$). (d) Asymmetry factor α as a function of θ . The asymmetry factor α is extracted from the same fit used in (b). It describes the relative contribution of homodyne detection over the DC magnetoconductance, depending on the alignment of the tip spin and Ti spin.

experienced by the Ti spin. The strength of B_1 consequently changes depending on the amplitude of the x' component of B_{tip} , while the y' component of B_{tip} provides a constant B_1 field (independent of the angle θ). Since Ω is proportional to the amplitude of the driving magnetic field, the driving factor in Eq. (2) varies accordingly [see the dashed line in Fig. 6(d)].

The detection of ESR signals in STM is based on the tunneling magnetoresistance effect. In STM, we measure the time-averaged tunneling current [14], which is detected by the applied DC and rf bias voltages [18]. The ESR signal detected by V_{DC} corresponds to the change in the time-averaged population of spin states detected by the component of the tip spin that is parallel to the quantization axis (the z' component of S_{tip}). The AC contribution to the ESR signal detected by V_{RF} results from the rectification of the applied V_{RF} by the spin precession at the same frequency [39,40]. This oscillating conductance is detected by the x' and y' components of S_{tip} . The ESR signal corresponding to the DC magnetoconductance shows four peaks when θ varies by 360° , since the detection is maximum when S_{tip} is parallel to the quantization axis of the Ti atom (S_{Ti}) and the driving is maximum when

B_{tip} is perpendicular to S_{Ti} . The AC magnetoconductance component (or homodyne detection) shows only two maxima in the ESR amplitude since both driving and detection are maximum when S_{tip} is perpendicular to S_{Ti} . The total ESR signal (AC and DC contributions) then results in the four maxima observed in Fig. 5(b).

Interestingly, when we assume that B_{tip} is exactly parallel with the spin polarization of the tip S_{tip} , we are unable to produce different height of the peaks shown in Fig. 5(b) using Eq. (2) (see the details in Sec. S8 in the Supplemental Material [17]). Instead, having B_{tip} slightly different from the S_{tip} direction, $B_{\text{tip}} \neq J(z) \langle S_{\text{tip}} \rangle$, based on their different origins, yields the best fit as given by the solid line in Fig. 5(b). The difference can occur from the non-negligible dipole interaction between the tip and the atom. Furthermore, while the spin polarization S_{tip} in the tunneling process is determined by the spin-resolved density of states at the Fermi level [36,41], the tip magnetization B_{tip} for the ESR driving fields results from the total occupied states of the tip spin. Such different origins describe well the results in Fig. 5(b) with different peak height. The rounded-out dips correspond to minima in

FIG. 6. ESR amplitude with model fits for three different tips: (a)–(c) model fits of ESR amplitude with data points obtained at $V_{DC} = 40$ mV, $I = 20$ pA, $V_{RF} = 10$ mV, and $T = 1.12$ K and (d)–(f) contribution of the z' component of S_{tip} (DC magnetoconductance, solid line) and driving factor $\Phi(\Omega)$ (dashed line) to the fit for tips 1–3, respectively. The results for tip 2 were measured at B_{ext} of 0.55 T and the results with the other two tips were measured at 0.7 T. We made the spin-polarized tip for ESR measurement at B_{ext} with $\theta = 50^\circ$ for tip 1, 70° for tip 2, and -10° for tip 3 [marked by arrow lines in (d)–(f)]. At those angles, the ESR signal appears maximum as we prepared the tip to yield large ESR signal amplitude I_1 .

the driving field, which corresponds to the minimum B_1 . On the other hand, the sharp dips in Fig. 5(b) appear at $\approx -18^\circ$ and $\approx 162^\circ$, where the DC magnetoconductance (depending on S_{tip}) is minimum and S_{tip} flips by 180° .

The amount of homodyne signals over the DC detection can be recognized from the asymmetry factor in Fig. 5(d). The asymmetric line shape of ESR signals originates from the homodyne detection of the tunneling current [18,32]. The maximum of the asymmetry factor, thus, corresponds to the maximum of the x' and y' components of S_{tip} , which allows us to determine the direction of S_{tip} in the laboratory frame.

E. Contributions of the spin-polarized tip to the ESR amplitude

We found a remarkable degree of reproducibility of the basic features of the B_{ext} field angle dependence of ESR signals for different tips and different Ti atoms. The ESR amplitudes as a function of the B_{ext} -field angle for three different tips are given in Figs. 6(a)–6(c).

We found that the ESR signals are almost at the maximum in amplitude at the angle at which we prepared the spin-polarized STM tip to measure ESR. This is due to the preparation procedure which aims to maximize the ESR signal at the preparation angle. As the total ESR amplitude is the result of the product between ESR driving and ESR detection [Eq. (2)], the strongest ESR signals are found at the angle where both driving strength and magnetoconductance are large. The ESR signal amplitude vanishes at certain angles, which explains why some spin-polarized tips do not

give any ESR signals empirically. The contributions of the z' component of S_{tip} for the ESR detection and the B_{tip} to the driving factor $\Phi(\Omega)$, as extracted from the fit, are depicted in Figs. 6(d)–6(f) by solid and dotted lines, respectively. While the driving factor is nonzero at every angle due to the finite y' components of B_{tip} , independent of B_{ext} angle, the z' component of S_{tip} is zero at certain angles, at which no ESR signals are observed. Based on this simple model [Eq. (2) and Supplemental Material [17]], the amplitudes of the ESR signals for different tips are well described as shown by the fit curves in Fig. 6.

We further confirmed that the direction of B_{tip} and S_{tip} varies for different tips. From the fit, we were able to distinguish the direction of S_{tip} and B_{tip} in three dimensions, where both S_{tip} and B_{tip} are off from the rotating plane of the external magnetic fields. In the case of tip 2 [Figs. 6(b) and 6(e)], the difference between the direction of B_{tip} and S_{tip} is $\approx 17^\circ$, which is bigger than other tips (less than $\approx 10^\circ$) (see Sec. S8 in the Supplemental Material [17]). This larger difference of B_{tip} and S_{tip} results in a less balanced distribution of the amplitude of the peaks. The detailed fitting parameters for three different tips are given in Sec. S8 in Supplemental Material [17].

This model demonstrates three critical points of the ESR-STM mechanism.

- (1) The direction of the spin polarization and the magnetic field by the tip can have a small mismatch depending on tips. Here, we derived those directions in three dimensions from the amplitude fit (Sec. S8 in Supplemental Material [17]).
- (2) The largest ESR signal is observed when the tip spin is aligned in a way to have adequate z' component of S_{tip}

and x' components of $\mathbf{B}_{\text{tip}}$. This ensures that ESR driving and detection are both effective.

(3) The DC magnetoconductance contributes more strongly to the ESR amplitude than the AC magnetoconductance at $V_{\text{RF}} = 10$ mV.

The analysis on the three-dimensional direction of $\mathbf{S}_{\text{tip}}$ and $\mathbf{B}_{\text{tip}}$ provides further understanding of the tip-induced magnetic environment.

IV. CONCLUSIONS

In this paper, we utilized a vector magnetic field to obtain a three-dimensional mapping of the g -factor anisotropy of Ti on MgO, and the results show a high degree of agreement with the multiplet calculation. The degree and directionality of this anisotropy highlight the sensitivity of the Ti spin to the substrate crystal field. Using this well-characterized surface spin through extensive measurements of the ESR frequency, amplitude, and line shape of a single Ti spin in vector mag-

netic fields, we fully characterized the tip-Ti coupling and determined the tip spin direction. Our paper further underlines the versatility of ESR-STM in a vector magnetic field as a highly sensitive magnetic probe to study the interaction between spin centers and their solid-state environments as well as the magnetic structure of the tip.

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