MAGNETIC RESONANCE

Hyperfine interaction of individual atoms on a surface

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Taking advantage of nuclear spins for electronic structure analysis, magnetic resonance imaging, and quantum devices hinges on knowledge and control of the surrounding atomic-scale environment. We measured and manipulated the hyperfine interaction of individual iron and titanium atoms placed on a magnesium oxide surface by using spin-polarized scanning tunneling microscopy in combination with single-atom electron spin resonance. Using atom manipulation to move single atoms, we found that the hyperfine interaction strongly depended on the binding configuration of the atom. We could extract atom- and position-dependent information about the electronic ground state, the state mixing with neighboring atoms, and properties of the nuclear spin. Thus, the hyperfine spectrum becomes a powerful probe of the chemical environment of individual atoms and nanostructures.

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T he hyperfine interaction between an electron and a nuclear spin provides insight into the electronic structure and chemical bonding of atoms, molecules, and solids. It is also key to realizing quantum operations of the nuclear spin (1-3). Although most experiments rely on ensemble measurement, detection and control of single nuclear spins is possible for diluted molecules in crystals (4), molecules in break junctions (3, 5), ion traps (2), and defects in solids (6, 7). Nevertheless, until now, no experimental tool allowed for imaging of the atomic-scale environment of the nucleus and simultaneous resolution of the hyperfine spectrum, which crucially depends on the local electronic structure.

Atomic resolution, along with atom manipulation, has been achieved by scanning probe methods, and they have been used to study the local electronic structure of atoms and molecules. Scanning probes allow chemical identification (8) and imaging of chemical bonds (9), and they provide access to the structure (10) and dynamics (11, 12) of electron spins. The nuclear properties detected in scanning tunneling microscopy (STM) include changes in vibrational (13) and rotational (14) motion, but the hyperfine interaction has not previously been resolved owing to a limited resolution in energy (15, 16).

Combining STM with electron spin resonance (ESR), as demonstrated for individual iron (Fe) (17, 18) and titanium (Ti) atoms (19, 20), potentially provides the required energy resolution. However, no hyperfine splitting was reported so far. For atoms that have low natural abundances of magnetic nuclei (such as Fe) or multiple magnetic isotopes (such as Ti), it is necessary to study a large number of individual atoms to establish the hyperfine physics. Here we present such a study, aided by a new understanding of the tunneling parameters (21) that improve the signal-to-noise ratio compared to previous ESR-STM experiments (17, 18).

Individual Fe and Ti atoms from sources that have natural isotopic abundance were deposited on two atomic layers of MgO grown on silver (22). First, we examined Fe atoms adsorbed onto an oxygen binding site of the MgO (23) (Fig. 1A). We resonantly excited transitions between the electronic ground state (spin-up) and the first excited state (spin-down) of the Fe atom by using ESR. We used a magnetic field \( B = 0.9 \) T and a temperature \( T = 1.2 \) K, unless stated otherwise. This excitation led to a change in tunnel current \( \Delta I \) when driven at the resonance frequency (17) (Fig. 1B). A magnetic tip was used for magneto- resistive readout, leading to different conductance for the two electronic states.

For 3.4% of Fe atoms (5 out of 147, see inset in Fig. 1B) investigated, the ESR peak was split by \( \Delta f = 231 \pm 5 \) MHz, where \( f \) is the frequency of the applied radio frequency voltage. We attributed this splitting to the presence of a nuclear moment \( I = \frac{1}{2} \) for \( ^{57} \)Fe (2.1% natural abundance). By contrast, the \( I = 0 \) isotopes, predominantly \( ^{56} \)Fe, showed no splitting. We could not distinguish different \( I = 0 \) isotopes and thus label them \(^{56} \)Fe for simplicity. Because the hyperfine splitting \( \Delta f \) is much smaller than the thermal energy \( k_B T / h = 25 \) GHz, where \( k_B \) is the Boltzmann constant and \( T \) is the Planck constant, the two nuclear states \( m_I = \pm \frac{1}{2} \) are occupied with equal probability. Thus, the \(^{57} \)Fe peaks each had half the ESR peak height of the single peak observed for \(^{56} \)Fe. Moreover, the simultaneous presence of two peaks indicates that the nuclear spin relaxation time was here much shorter than the time scale of the measurement (1 ms) (22).

For the magnetic field used here, the electronic Zeeman energy is large compared to the hyperfine interaction. Because the Fe atom on MgO shows a large out-of-plane magnetic anisotropy, the electron spin is quantized along the out-of-plane direction \( z \) (23). Thus, the nuclear spin was quantized along \( z \) as well, leading to the spin Hamiltonian (24)

\[
H = g_B \mu_B B_z S_z + A_J J_z S_z + \text{hf}
\]

where \( \mu_B \) is the Bohr magneton and \( S_z \) and \( J_z \) are the \( z \)-axis spin operators for the electron and nuclear spin, respectively. Parameters \( g_B \) and \( A_J \) are the \( z \)-components of the electron g-factor and the hyperfine coupling constant, respectively. \( B_z \) is the \( z \)-component of the magnetic field. The very small nuclear Zeeman energy is neglected here.

When determining the eigenstates of Eq. 1, the spins can either be aligned or anti-aligned with the magnetic field to give product states \( |m_S, m_I \rangle \), where \( m_S \) and \( m_I \) are the electron and nuclear quantum numbers (Fig. 1C). Transitions occurred between the \( m_S = \pm 2 \) electronic states \( \Delta m_S = \pm 4 \) (17) and left the nuclear spin state unchanged \( \Delta m_I = 0 \), leading to one resonance peak for \(^{56} \)Fe. The spectra were centered at frequency \( f_0 \) given by the Zeeman energy \( h f_0 = g_B \mu_B B_z m_S + \text{hf} \). The two frequencies observed for \(^{57} \)Fe in Fig. 1B differed because of the relative alignment of the electron and nuclear spin, to give a peak splitting \( \Delta f = \Delta m_I \Delta m_S A_J = 2A_J \mu_B B_z \), where \( A_J = 1 \) (24).

In contrast to that of Fe, the hyperfine interaction of Ti atoms was more complex and reflected changes in the local electronic environment (24). The Ti atoms studied here were hydrogenated (19), resulting in an electronic spin of \( \frac{1}{2} \) that lacked magnetic anisotropy. Thus, to good approximation, the electron spin followed the magnetic-field direction (19, 20). The hyperfine spectra for Ti located on a bridge binding site \( \text{Ti}_B \) of MgO (20) (Fig. 2) showed 2\( f \) + 1 peaks, one for each nuclear spin state, resulting in six peaks for \(^{48} \)Ti \( (I = \frac{3}{2}, 7.4\% \) natural abundance), eight peaks for \(^{49} \)Ti \( (I = \frac{7}{2}, 5.4\%) \), and a single peak for the nuclear spin–free isotopes, predominantly \(^{46} \)Fe \( (I = 0, 73.7\%) \). We found a splitting \( \Delta f \) between adjacent peaks of \( \approx 47 \) MHz for both \(^{47} \)Ti and \(^{48} \)Ti, implying that their nuclear gyromagnetic ratios were equal (see section 2 in (22)). For all investigated atoms, we found no appreciable dependence of the hyperfine splitting on the magnetic field caused by the proximity of...
the tip (19) nor on the local electric field induced by the dc bias voltage.

In contrast to ensemble measurements, the binding site of individual atoms could be determined from STM images, and the atom could be moved among binding sites by using atom manipulation. We moved a $^{52}$Ti atom to different binding sites (Fig. 3A). We observed a pronounced reduction of the splitting $\Delta f$ to $\sim 10$ MHz (Fig. 3B) when the Ti atom was moved from a bridge to an oxygen site (TiO). The larger splitting was restored by moving the same atom back to a bridge binding site. In Fig. 3C, we show the exact position of the atoms obtained from Fig. 3A and show density functional theory (DFT) calculations (22) of the respective electronic ground state. The statistics for different atoms on the same type of binding site (Fig. 3D) revealed a small, but reproducible, difference in $\Delta f$ for the two inequivalent bridge binding sites. This difference was caused by different values of $g_x \neq g_y$ and $A_x \neq A_y$ (resulting from the low symmetry of the bridge binding site) along with a magnetic field direction $B_x \neq B_y$ [Fig. 3C and section 1 in (22)].

Hyperfine spectra for both isotopes of TiO are shown in high resolution in Fig. 3E. In addition to the strong decrease in $\Delta f$ compared with that for TiB, the interval between peaks as well as their amplitudes were nonuniform. To describe the spectra, we generalize the hyperfine Hamiltonian in Eq. 1 to

$$H = H_{zz} + H_{HF} + H_{NQ}$$

Here, the electron Zeeman term $H_{zz} = \mu_B g_i S_i$ and the hyperfine term $H_{HF} = \sum_{i=1}^{2} A_i I_i S_i$ were generalized to include the $x$ and $y$ spin components, needed for electronic spins lacking strong isotropy (19), and the hyperfine interaction was allowed to have anisotropy. Moreover, $H_{NQ} = \sum_{i=1}^{2} P_i I_i^2$ is the nuclear electric quadrupole interaction, caused by the electric field gradient at the position of the nucleus (24), where $P_i$ are the components of the nuclear electric quadrupole tensor (22). This quadrupole term is irrelevant for $I = \frac{1}{2}$ systems, as in the case of Fe (24). Using the known symmetry of the system, only three fit parameters, $A_x A_y = A_0$, and $P_x$ were required to give good fits to the complex hyperfine spectrum of TiO (22).

Simulated ESR spectra of the experimental data obtained by using EasySpin (25) are superimposed on the data in Fig. 3E. The fits reflect that the hyperfine and the nuclear quadrupole interaction have comparable energies for TiO, resulting in peaks that are irregularly spaced because they are not well approximated by eigenstates of either operator alone. Furthermore, these measurements allowed us to determine the ratio of the nuclear quadrupole moments of $^{48}$Ti/$^{49}$Ti $\approx 0.79$. The excellent agreement with ensemble measurements ($^{48}$Ti/$^{49}$Ti $\approx 0.82$ (26)) shows the fidelity of the model and that good accuracy was obtained with this limited number of fit parameters.

Although the electric quadrupole interaction changed the peak intensities and spacings for TiO, the overall reduction in $\Delta f$ compared to that for TiB was caused by the reduction in the hyperfine coupling constant $A$. We consider here two contributions (24). The first is the isotropic Fermi contact term originating from a finite spin density of unpaired $s$ electrons at the nucleus induced by interaction with the $d$ electrons. The second is the anisotropic magnetic dipolar interaction of the nuclear spin with the surrounding $d$ electrons, which depends on the orbital symmetry (27). The observed changes in $\Delta f$ for the different binding sites of Ti were caused by the occupation of different orbitals in the magnetic ground state of the atom (Fig. 3C). We found a larger Fermi contact contribution for TiB (+50 MHz) compared with that for TiO (+19 MHz), presumably caused by a difference in covalency (24) [section 2 in (22)].

More importantly, the three spatial components of the dipolar contribution changed in magnitude and sign for the different binding sites. Because the magnetic field was applied

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**Fig. 1.** Hyperfine interaction studied by ESR in a scanning tunneling microscope. (A) Experimental setup showing different single Fe atoms on a bilayer MgO film on Ag(001) in an STM ($B = 0.9$ T, $B_z = 0.1$ T, and $T = 1.2$ K). ESR was performed by applying a radio frequency voltage ($V_{RF}$) to the tunneling junction (17, 18). SP, spin-polarized; $V_{DC}$, direct current voltage. (B) ESR spectra of the change in tunnel current for different Fe isotopes (top). The blue line shows Fe that has zero nuclear spin (likely $^{56}$Fe; see main text). The orange line shows $^{57}$Fe with nuclear spin $I = \frac{1}{2}$. Spectra were normalized to unity for $^{56}$Fe and given in arbitrary units (a.u.). Electron Zeeman energy gives the center frequency $f_0$, here 19.89 GHz for $^{56}$Fe and 19.87 GHz for $^{57}$Fe (tunnel conditions: $I_{sat} = 12$ pA, $V_{DC} = 60$ mV, and $V_{RF} = 60$ mV). The inset shows the peak splitting $\Delta f$ for five different $^{57}$Fe atoms. The solid line indicates the error-weighted mean. Shown at the bottom are topographic images of both atoms. (C) Schematic of the energy levels $E$ of the $^{56}$Fe atom, compared to those of $^{57}$Fe, including hyperfine interaction as a function of the external magnetic field $B$ and the hyperfine constant $A$ (the small nuclear Zeeman energy was neglected).

**Fig. 2.** Hyperfine interaction for titanium on a bridge binding site. On the left are ESR spectra for $^{48}$Ti (blue, nuclear spin $I = 0$), $^{47}$Ti (orange, $I = \frac{1}{2}$), and $^{49}$Ti (yellow, $I = \frac{3}{2}$). The inset shows the bridge binding site. On the right are STM images for each atom. Experimental conditions for $^{48}$Ti: $f_0 = 23.03$ GHz, $I_{sat} = 8$ pA, $V_{DC} = 40$ mV, and $V_{RF} = 30$ mV; for $^{47}$Ti: $f_0 = 22.99$ GHz, $I_{sat} = 8$ pA, $V_{DC} = 40$ mV, and $V_{RF} = 30$ mV; and for $^{49}$Ti: $f_0 = 22.69$ GHz, $I_{sat} = 20$ pA, $V_{DC} = 60$ mV, and $V_{RF} = 40$ mV.
nearly in-plane (Fig. 1A), the in-plane components $A_x$ and $A_y$ contributed the most to $\Delta f$. In the case of TiO, the dipolar contribution added to the Fermi contact part for one of the two components ($A_x = +61$ MHz; $A_y = +29$ MHz). By contrast, for TiB, both in-plane directions opposed the Fermi contact interaction, resulting in $A_x = A_y = +10$ MHz. As a result, $\Delta f$ is smaller for TiO than for TiB. The strength of the hyperfine interaction and the importance of quadrupole interaction revealed the profound change in the chemical environment of the Ti atom upon moving it from a bridge site to an oxygen site: Modeling the hyperfine interaction and taking the DFT ground state into account, we find that the bonding with oxygen reduces the electron spin density at the Ti nucleus for TiO [−1 instead of −2.8 atomic units for TiB (22)]. Moreover, the radial spread of the spin-polarized orbital (r−3) can be deduced from the hyperfine splitting and the electric quadrupole contribution, which lies at −0.5 Å−3 for both binding sites (22).

Hyperfine spectra can also reveal changes in the magnetic environment, as we demonstrate here using assembled structures of Ti atoms. Figure 4A shows a 47TiB atom with a nuclear spin $I = \frac{1}{2}$ that was moved to a position ~7 Å from a 47TiO atom ($I = 0$). Because of the exchange interaction between the electronic spins, an electronic singlet-triplet system was formed (right panel of Fig. 4B and section 3 in (22)) (19, 20). The Zeeman term split the triplet states ($T_2$, $T_0$, and $T_1$), whereas the energies of both the singlet $S_0$ and the triplet state $T_0$ remained independent of magnetic field.

Analogously, the hyperfine interaction did not split either $S_0$ or $T_0$, and for the $T_2$ and $T_1$ states, the splitting remained the same as for the single atom (Fig. 4B). Thus, the hyperfine splitting for the $T_2$-$T_1$ transition, which involved one of the magnetic field–dependent states ($T_0$), decreased to only 27.2 ± 0.4 MHz, roughly half the value of the isolated Ti case (Fig. 4C). Accordingly, the hyperfine splitting of the singlet-triplet transition ($S_0$-$T_0$) in Fig. 4C was essentially zero (less than our ~10 MHz linewidth). These transitions allowed us to probe the polarization of the coupled-atom states and to quantify the degree of state mixing to 87% in the singlet state [section 3 in (22)]. Here $A$ remained constant, and instead, the electronic spin magnetization was changed (20). This Ti dimer structure showed that the collective properties that emerged in a correlated multispin structure yielded characteristics sharply different than those of the constituents.

REFERENCES AND NOTES
22. Materials and methods are available as supplementary materials.

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SUPPLEMENTARY MATERIALS
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Hyperfine interaction of individual atoms on a surface

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Hyperfine spectra of surface atoms
The interaction of nuclei with nonzero spin with electron spins creates small electronic energy. With a scanning tunneling microscope tip, Willke et al. measured these hyperfine interactions for iron and titanium atoms that were manipulated on a magnesium oxide surface. The tip was also used to measure electron paramagnetic resonance spectra. The hyperfine structure of single atoms was sensitive to the binding site of the atom as well as its position relative to other magnetic atoms.

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