Local Electronic Structure and Dynamics of Muon-Polaron Complexes in Fe$_2$O$_3$

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We perform detailed muon spin rotation ($\mu$SR) measurements in the classic antiferromagnet Fe$_2$O$_3$ and explain the spectra by considering dynamic population and dissociation of charge-neutral muon-polaron complexes. We show that charge-neutral muon states in Fe$_2$O$_3$, despite lacking the signatures typical of charge-neutral muonium centers in non-magnetic materials, have a significant impact on the measured $\mu$SR frequencies and relaxation rates. Our identification of such polaronic muon centers in Fe$_2$O$_3$ suggests that isolated hydrogen (H) impurities form analogous complexes, and that H interstitials may be a source of charge carrier density in Fe$_2$O$_3$.

The semiconducting transition metal oxide (TMO) α-Fe$_2$O$_3$ is a prototypical antiferromagnet whose magnetic properties are still actively studied [1,2]. It is also a promising photoanode for solar water splitting [3,10] due to its natural abundance, non-toxicity and 2.1 eV bandgap that allows for efficient visible light absorption. However, photoelectric device performance is significantly hindered by the formation of small polarons: excess electrons localize on Fe ions and cause both a change in valence from Fe$^{2+}$ to Fe$^{3+}$ and a local lattice distortion [10–12]. As a result, conduction occurs via thermally activated polaron hopping [14–15] rather than efficient band-type transport. Efforts are being made to improve device performance by studying the impact of dopants such as Sn, Ti and Si on polaron transport [17,20], however, little consideration is given to unintentional dopants such as hydrogen (H). Incorporated during growth and post-processing, H is one of the most ubiquitous impurities in semiconductors [21,23], and can significantly influence their electronic properties. Since isolated H is extremely hard to study directly, most information about its dopant characteristics comes from the study of muonium (Mu=[$\mu^+e^-$]), a light H analog with virtually identical electronic structure, which is experimentally accessible via the muon-spin-rotation ($\mu$SR) technique [24–27]. Recent $\mu$SR studies reported polaronic Mu centers in non-magnetic TMOs such as SrTiO$_3$ and TiO$_2$ [28,30], in which an oxygen-bound, positive muon and a small polaron located on a neighboring TM ion form an overall charge-neutral complex, suggesting that isolated H defects form analogous H-polaron centers. Recently, muon-polaron complexes have been shown to exist in the antiferromagnet Cr$_2$O$_3$ [31]. In a crucial distinction to non-magnetic TMOs however, the excess electron spin strongly couples to the unpaired $d$ electrons of the Cr host, resulting in a $\mu$SR signal that is difficult to distinguish from the usual signal of the positive charge state (i.e. the bare muon), and thus may be easily misidentified. Therefore, “hidden” charge-neutral muon states need to be carefully considered when using the muon as a sensitive local probe of magnetism in insulating magnets, especially TMOs [32,33].

Here we report a detailed $\mu$SR study on α-Fe$_2$O$_3$ and identify, supported by density functional theory (DFT), several muon-polaron complex configurations that are very close in energy. Expanding on early work [34–40], we are able to consistently interpret the complicated $\mu$SR spectra at low temperatures ($T$) in terms of transitions between various complex configurations and local muon hopping. Our results show that muon-polaron complexes in Fe$_2$O$_3$ significantly influence the $\mu$SR signals, demonstrating that in order to relate experimental data to intrinsic magnetic properties, both muon and polaron dynamics have to be considered. Finally, the muon-polaron complex dissociates above $\sim$200 K, strongly suggesting that analogous H centers may act as electron donors.

α-Fe$_2$O$_3$ has the corundum structure (space group R3c), is weakly ferromagnetic below $T_N$ = 948 K, and becomes antiferromagnetic below the Morin temperature $T_M \sim$ 260 K, with spins aligning pairwise antiparallel along the rhombohedral 111 axis ($\hat{c}$ axis) [Fig. 1 inset 1]. Focusing on $T < T_M$, we carried out $\mu$SR experiments at 2.2 $< T <$ 265 K in zero external magnetic field (ZF) in the LAMPF spectrometer at TRIUMF (Canada). Spin polarized, positively charged muons were implanted into a natural single crystal (SurfaceNet, Germany), with the initial muon polarization aligned within 5° normal to the $\hat{c}$ axis. The subsequent muon decay (lifetime $\tau_\mu = 2.2 \mu$s) enabled the observation of the time evolution of its spin polarization via the anisotropic emission of the decay positrons [32]. Due to spin precession in local magnetic fields $\mathbf{B}_i$ from ordered Fe moments surrounding various muon stopping sites, up to three coherent oscillation frequencies $f_i = \gamma_\mu/2\pi |\mathbf{B}_i|$ were observed, where $i = 1–3$ labels the signal components and $\gamma_\mu = 2\pi \cdot 135.5$ MHz/T is the muon gyromagnetic ratio [Fig. 1(a)]. $f_1$ (•) is...
detected at all $T$ up to $T_M$, whereas $f_2$ (●) and $f_3$ (▲) are only observed up to 235 K and 90 K, respectively, indicating that each $f_i$ originates from sites that are energetically inequivalent. The spectra are fit to a sum of exponentially damped oscillatory signal components $S_i(t)$

$$S_i(t) = a_i \cos(2 \pi f_i t + \phi_i) \exp(-\lambda_i t),$$

where $a_i$, $f_i$, $\phi_i$ and $\lambda_i$ are the signal amplitude, frequency, phase shift and relaxation rate, respectively. Remarkably, none of the frequencies simply decrease with increasing $T$ as they would if they followed the magnetic order parameter $[41]$. Instead, they display distinct step-like features. Likewise, the amplitudes and relaxation rates vary strongly with $T$ [Fig. 1(b) and (c)]. In the following, we explain the data by considering muon diffusion, site transitions and charge-neutral complexes.

First, we discuss the most stable signal, $S_1$ [Fig. 1(●)], which we attribute to the positive charge state. The discontinuity around 80 K in $f_1$ is explained in terms of local hopping on a ring of adjacent, electrostatically equivalent sites [Fig. 2(a)]. This was also observed in isomorphic Cr$_2$O$_3$ [31] and has been proposed for Fe$_2$O$_3$ [31][36]. In Cr$_2$O$_3$, the magnetic structure ($\uparrow\uparrow\uparrow\downarrow\downarrow$) breaks the inversion symmetry $(\mathbf{B}(\mathbf{r}) = -\mathbf{B}(-\mathbf{r}))$ such that sufficiently fast local hopping leads to a complete cancellation of the internal field and subsequent loss of the oscillatory signal, while in Fe$_2$O$_3$ ($\downarrow\uparrow\uparrow\downarrow\downarrow$), $\mathbf{B}(\mathbf{r}) = \mathbf{B}(\mathbf{r})$, and fast hopping only causes a cancellation of the radial in-plane component ($\downarrow\mathbf{c}$) [31], resulting in the drop in $f_1$ and the peak in $\lambda_1$ around 80 K. Our simulation of the muon polarization function $[31][42]$ based on (1) a simple parametrization $L(T)$ of the $T$-dependence of the order parameter $[34]$ [Fig. 1(a), gray dashed line] and (2) assuming local hopping between adjacent sites with Arrhenius-like activation (using an activation energy $E_1 = 55$ meV, prefactor $A_1 = 2 \times 10^{12}$ Hz and angle $\theta_1 = \angle(\mathbf{B}_1, \mathbf{c}) = 6.1^\circ$) yields good agreement (solid red lines) with the step in $f_1$ and shape, position and magnitude of the peak in $\lambda_1$.

We attribute the remaining two signals, $S_2$ and $S_3$, to charge-neutral muon states, a scenario supported by DFT as outlined below. We analyze their more complex behavior with the simplifying assumptions that (1) the internal fields causing precession at $f_2$ and $f_3$ are oriented along the $\hat{c}$ axis, and (2) at a given site, the internal field follows $L(T)$. We propose that the unusual increase of $f_3$ with increasing $T$ is due to a thermally excited state with frequency $f_{3B}$. At 2.2 K, only the ground state with $f_{3A} = 222.1$ MHz is occupied, however, with rising $T$, the excited state becomes populated, with the mean occupation probability described by the energy difference $\Delta E_3 = E_{3B} - E_{3A}$ and a Boltzmann factor $P_{E3}(T) = e^{(-\Delta E_3/k_B T)}/[1 + e^{(-\Delta E_3/k_B T)}]$ [28], leading to a mean frequency $f_3(T) = [(1 - P_{E3}(T)) f_{3A} + P_{E3}(T) f_{3B}] \cdot L(T)$. For $f_{3B} = 241.7 \pm 1.0$ MHz and $\Delta E_3 = 5.4 \pm 1.0$ meV, this expression yields good agreement with the data [Fig. 1(a), dashed blue line], and allows for a prediction of the expected $T$-dependence beyond the temperatures where it is observed. The peak in $\lambda_3$ around 30 K is consistent with the proposed $f_{3A} \leftrightarrow f_{3B}$ transitions and indicates the presence of a small energy barrier $\sim 5$ meV.

Next, we address the disappearance of $f_3$ above 100 K, the upturn in $f_2$ above 120 K, and the increase in $a_2$. We propose that approaching 100 K from below, muons initially in $f_3$ are able to overcome a barrier $\Delta E_B$ and start to transition into the lower-energy $f_2$ state, causing $f_3$ to vanish. With further increasing $T$, the reverse transition from $f_2$ to $f_3$ also becomes accessible on the scale of $\tau_\mu$, resulting in a dynamic joint state of $f_2$ and

![FIG. 1. Results of fits of the ZF-µSR spectra to up to three oscillatory components $S_i(t)$ (Eqn. 1), with $i = 1$ (●), 2 (●), 3 (▲). Solid and dashed lines represent models as described in the main text. (a) frequencies $f_i$, (b) amplitudes $a_i$ and (c) relaxation rates $\lambda_i$. Insets: (1) Primitive unit cell of Fe$_2$O$_3$. (2) Phase shift $\phi_i$. (3) Proposed schematic energy landscape of the muon sites associated with $f_2$ and $f_3$ (not to scale).]
$f_3$ [blue and orange dashed lines] with combined amplitude, increased relaxation and increasing (occupation-averaged) frequency [Fig. 1(b), inset 3]. Finally, above $\sim 160\, K$, the transition rate in both directions is sufficiently fast that a Boltzmann distribution is established, since $\Delta E_B$, which suppresses transitions at lower $T$, is no longer relevant. We model the data in two steps. First, the data above $170\, K$ is fit to a Boltzmann weighted frequency $f_{23}(T) = [(1 - P_{E23}(T))f_2 + P_{E23}(T)f_3(T)]$ [dotted orange line], from which $\Delta E_{2+3} = E_3 - E_2 = 16.5 \pm 2.0\, meV$ is obtained. Then, $\Delta E_B$ is taken into account by simulating the muon polarization assuming a thermally activated $f_2 \leftrightarrow f_3$ transition with energy barrier $\Delta E_B = 95 \pm 25\, meV$ and prefactor $A_{23} = 4.5 \times 10^{11}\, Hz$, yielding excellent agreement with the frequency step and the associated peak in $\lambda_2$ [Fig. 1 solid orange lines].

Lastly, we address the pronounced dip in the phase $\phi_1$ [Fig. 1(a), inset 2], the increase in $\alpha_1$, the disappearance of $f_2$, and the sharp increase in $\lambda_2$, all occurring around $225\, K$. Together, the features are clear evidence for a thermally activated transition of muons from $f_2$ to $f_1$. Assuming a transition rate of the form $\Lambda(T) = A_{2-1}\exp(-\Delta E_{2-1}/k_B T)$, the data are consistently described [Fig. 1 brown lines] using a simple transition model [44], Eqs. C1-C4 in Ref. [31] with shared parameters $\Delta E_{2-1} = 0.35 \pm 0.05\, eV$ and $A_{2-1} = 6 \times 10^{14}\, Hz$.

With that, all the major features in Fig. 1 are explained in terms of local muon hopping, thermally accessible excited states, dynamic population of metastable states separated by a barrier, and, finally, a transition of metastable $f_2$ states to the apparent ground state $f_1$.

Now we turn to DFT to search for muon stopping sites consistent with the observed behavior. LDA+U calculations were carried out using VASP [15][18]. The $\mu^+$ was modeled as a H nucleus, embedded within an 80-atom $2 \times 2 \times 2$ rhombohedral supercell. A site search procedure similar to Ref. [31] was carried out for both the positive and neutral charge states; additionally, negatively charged states were considered [details and structure files in 19]. For each energetically distinct candidate site (C) [50], the precession frequency $f_{\text{dir}}$ in the combined hyperfine and dipolar fields was calculated [Table 1]. A single stable candidate site for the positive charge state ($C^+$), four possible sites for the charge-neutral state ($C_0^-$-$C_0^+$) and two configurations for the negative charge state ($C^- & C_2^-$) were obtained, all with the muon stopping $\sim 1\, A$ away from an oxygen. Independent of the charge state, the muon localizes close to the electrostatic potential minimum of the undistorted cell [Fig. 2(a), blue isosurface]. Note that despite rapid transitions between different sites, the muon does not leave the confinement of one such “muon cage” bounded by two 60° rotated oxygen triangles - a site change to an adjacent cage would result in a sign change of the local $\mathbf{B}$, leading to a cancellation of internal field and subsequent signal loss, which is not observed for $T < T_M$ [51].

We associate $S_1$, the only signal observed up to $T_M$, with $C^+$ [Fig. 2(b)], in good agreement with $f_{\text{dir}}^{C^+}$ [51]. Additionally, in analogy with Cr$_2$O$_3$ [E3 in Ref. [31]], the close proximity of adjacent electrostatically equivalent sites strongly supports the $T$-dependence of $f_1$ being due to positive muons undergoing locally restricted motion within a given muon cage.

In $\mu$SR studies of magnetic materials, usually only the positive charge state is considered. However, it is clear that in Fe$_2$O$_3$, as in Cr$_2$O$_3$, the single $C^+$ site cannot explain the data and other charge states have to be taken into account. The neutral $C_0^-$-$C_0^+$ can be characterized as muon-polaron complexes: the bound electron predominantly localizes on a nearby Fe ion to form a small polaron, occupying an empty minority spin $t_{2g}$ orbital and changing the Fe valence from $\text{Fe}^{3+}$ (3$d^6$) to $\text{Fe}^{2+}$ (3$d^7$) [Fig. 2(c)-(e)]. The electron localization is aided by the presence of the positive muon bound to an adjacent oxygen, forming an overall charge-neutral muon-polaron complex $\text{Fe}^{2+}(\mu^-)$ [52]. In contrast to non-magnetic materials, the spin of the bound electron is strongly coupled to the unpaired 3$d$ electrons of the Fe host; as a re-
sult, the spin degree of freedom typical of paramagnetic 

Mu centers is lost, and only a single frequency rather than the characteristic multiplet is displayed.

In a given muon cage, there are two distinct Fe positions belonging to different magnetic sublattices: axially above and below [Fig. 2(a), light brown], or equatorially around the cage in a buckled plane [Fig. 2(a), dark brown]. Each of the equatorial Fe is bound to two oxygens that make up the cage, with one bond slightly longer than the other. Focusing on the three lowest-energy \( \{ \text{C}_1 \} \), \( \{ \text{C}_2 \} \) and \( \{ \text{C}_3 \} \) sites, the electron is predominantly localized on an axial Fe [Fig. 2(c)], whereas for \( \{ \text{C}_2 \} \) and \( \{ \text{C}_3 \} \), the polaron is mainly on an equatorial Fe, with the muon bound either to the oxygen forming the long (\( \{ \text{C}_2 \} \)) or the short (\( \{ \text{C}_3 \} \)) bond [Fig. 2(e)]. We propose that \( \{ \text{C}_1 \} \)-\( \{ \text{C}_2 \} \) can explain the \( S_2 \) and \( S_3 \) signals as follows: transitions between \( \{ \text{C}_2 \} \) and \( \{ \text{C}_3 \} \) mainly correspond to the muon hopping between the two oxygens that are both bound to the Fe\(^{2+} \) (polaron) ion [Fig. 2(f)]. Noting that the presence of the extra electron significantly distorts the lattice and decreases the distance and thus the barrier between the two sites, this provides a plausible mechanism for the low-T dynamics (\( f_{3A} \leftrightarrow f_{3B} \)), and renders \( \{ \text{C}_2 \} \) and \( \{ \text{C}_3 \} \) good candidate sites for \( f_{3A} \) and \( f_{3B} \), jointly explaining \( S_3 \). \( \{ \text{C}_1 \} \) is assigned to \( S_2 \), supported by its low energy and good agreement in measured and calculated frequency. Given the uncertainties inherent to DFT [53], there is good agreement between DFT and all observed frequencies [Table I]. Considering the proposed \( f_2 \leftrightarrow f_3 \) transitions, this state assignment suggests that for \( T \gg 100 \) K, transitions between \( \{ \text{C}_1 \} \) and \( \{ \text{C}_2 \} \) occur, implying that polaron dynamics rather than muon hopping drives this dynamic process [Fig. 2(g)]. The energy barrier \( \Delta E_B \approx 95 \pm 25 \text{ meV} \) is attributed to both the small polaron hopping (aided by the presence of the muon for the two Fe ions involved) and a spin contribution (of the order of \( \sim k_B T N = 82 \text{ meV} \)) accounting for the polaron hopping between magnetic sublattices. Note that the energies of \( \{ \text{C}_1 \} \) and \( \{ \text{C}_2 \} \) are very close [Table I], enabling the back-and-forth transitions postulated above, with the energy difference matching closely \( \Delta E_{2+3} \). In sharp contrast, the different complex configurations in \( \text{Cr}_2\text{O}_3 \) are well separated in energy [31], and neither unusual dynamics, nor frequencies deviating from the order parameter are observed. The difference in energy separation (and consequently, dynamic behavior) is attributed to the strength of the polaron-induced Jahn-Teller (JT) distortion [53]. \( \text{Cr}^{2+} \) with 3d\(^4 \) (high spin) is strongly JT-active, whereas \( \text{Fe}^{2+} \) with 3d\(^6 \) (high spin) is only weakly JT-active.

Lastly, we discuss the negative \( (\text{C}^-) \) charge state, comprised of an oxygen-bound muon and two polarons, located on both axial and equatorial Fe ions \( \{ \text{C}_1 \} \) shown in Fig. 2(h)]. DFT in large (270-atom) supercells suggest that \( \{ \text{C}_1 \} \) is lower in energy than \( \{ \text{C}_2 \} \) and a separated polaron; likewise, \( \{ \text{C}_0 \} \) is lower in energy than \( \{ \text{C}_1 \} \) and a separated polaron [49], indicating that \( \{ \text{C}^- \} \) is the lowest energy state if sufficient excess electrons are available. Also, \( f_{3\text{AB}} \) is close to \( f_1 \), rendering \( \{ \text{C}^- \} \) an alternative candidate for \( S_1 \). However, we consider the scenario where \( S_1 \) originates from \( \{ \text{C}_1 \} \) rather than \( \{ \text{C}^- \} \) unlikely, since (1) at low \( T \), polarons are highly immobile, and while it is conceivable (and necessary to explain the data) that a thermalizing muon captures a single electron, it is implausible that all other muons capture two electrons to form \( \{ \text{C}^- \} \) and no \( \{ \text{C}^+ \} \) is formed at all. (2) Above 250 K, \( S_1 \) represents the complete signal, and while the Boltzmann factor favors \( \{ \text{C}^- \} \), the overwhelming degeneracy of free polaron states away from the muon is expected to dominate. Thus, we are confident in assigning \( S_1 \) to \( \{ \text{C}^+ \} \).

This assignment directly implies that the \( f_2 \rightarrow f_1 \) transition around 225 K corresponds to a charge-state transition from neutral to positive, which we characterize as a complex dissociation [30], i.e. a separation of the polaron and the oxygen-bound muon, rather than an ionization of the bound electron to the conduction band. Then, \( \Delta E_{2+1} \approx 0.35 \text{ eV} \) corresponds to the barrier the polaron has to overcome to dissociate from the positive muon. Notably, \( \Delta E_{2+1} \) is larger than barrier estimates of 0.1 – 0.2 eV for “free” polaron hopping [10 14 18 29], indicating that the muon acts as a trap and thus lowers polaron mobility [20]. By the well established analogy between \( \mu^+ \) and a proton [23–27], these results indicate that isolated H impurities in \( \text{Fe}_2\text{O}_3 \) form corresponding \( \text{Fe}^{2+} (\text{OH})^- \) complexes. While the dynamic behavior, especially at low \( T \), is expected to be different owing to the mass difference (\( m_{\mu} \approx \frac{1}{9} m_p \)), the electronic structure (which depends on the \textit{reduced} electron mass) is virtually identical. Likewise, the observed complex dissociation, characterized by the polaron hopping away, is expected to be comparable for H-polaron complexes, suggesting that at room temperature, interstitial H contributes “free” polarons and thus increases the carrier density, while simultaneously acting as a trap, decreasing overall carrier

| CS | Site | \( f_{\text{ab}} \) [MHz] | \( \theta \) [\degree] | \( \Delta E \) [meV] | \( f_{\text{exp}} \) [MHz] |
|----|------|-----------------|----------------|--------------|----------------|
| +  | \{C\} | 228.0           | 7.6            | 0            | 224.4 (\( f_1 \)) |
| 0  | \{C\} | 214.5           | 8.5            | 0            | 208.9 (\( f_2 \)) |
|    | \{C\} | 225.9           | 7.3            | 12.5         | 222.0 (\( f_{3A} \)) |
|    | \{C\} | 239.5           | 7.1            | 37.2         | 241.7 (\( f_{3B} \)) |
|    | \{C\} | 259.1           | 6.7            | 50.6         |                 |
| -  | \{C\} | 225.3           | 7.9            | 0            |                 |
|    | \{C\} | 211.0           | 8.7            | 3.7          |                 |

TABLE I. Candidate muon stopping sites C obtained with DFT for the positive, neutral and negative charge states (CS): calculated precession frequencies \( f_{\text{ab}} \), angle \( \theta = \angle (\text{B}, \text{c}) \) and energy \( \Delta E \) relative to the ground state of each charge state. \( f_{\text{exp}} \) lists observed frequencies next to proposed sites.
mobility.

In summary, we present a detailed μSR study of Fe$_2$O$_3$, and consistently explain the observed spectra by considering charge-neutral muon-polaron complexes, with different complex configurations providing an intuitive explanation for magnetically distinct sites that are close in energy. The unusual T-dependences of the observed frequencies and relaxation rates are well described by transitions between these complex configurations, demonstrating that the presence of muon-polaron complexes in magnetic materials can alter the observed μSR signals such that they not only reflect the intrinsic magnetic properties, but also both muon and polaron dynamics. The identification of charge-neutral Fe$^{2+}$ (O$\mu^-$) complexes clearly shows that Cr$_2$O$_3$, the first magnetic material where muon-polaron complexes were observed [31], is not an isolated case. Analogous complexes with similarly inconspicuous signals likely exist in other insulating magnets, in particular in TMOs where the multivalent character of the TM ions facilitates polaron formation. We contend that a careful consideration of such charge-neutral muon states (and associated local dynamics, as demonstrated here), in conjunction with DFT, can significantly enhance the muon’s power as a sensitive local probe of magnetism. Lastly, the presence of polaronic muon centers suggests that H impurities form analogous Fe$^{2+}$ (OH)$^-\mu^-$ complexes at low T, but dissociate at room temperature, indicating that interstitial H in Fe$_2$O$_3$ increase the charge carrier density while simultaneously lowering the polaron mobility.

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[51] Long range muon diffusion in Fe$_2$O$_3$ leading to signal cancellation does occur [34], however only above $\sim 400$ K.

[52] Charge-neutral relative to Fe$^{3+}$O$^{2-}$ + $\mu^+$, i.e. the additional charge from the muon is compensated.

[53] The need to choose a Hubbard $U_{\text{eff}}$ ($U_{\text{eff}} = 4$ eV for results above) is the dominant source of uncertainty. Varying $U_{\text{eff}}$ between 3 − 6 eV, we find that although the numerical values vary as a function of $U_{\text{eff}}$, the qualitative behavior remains robust throughout 3 − 5 eV, the range typically employed for Fe d states (see [49]).

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