Candidate Source of Flux Noise in SQUIDs: Adsorbed Oxygen Molecules

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(Received 18 April 2015; published 14 August 2015; corrected 17 November 2015)

A major obstacle to using superconducting quantum interference devices (SQUIDs) as qubits is flux noise. We propose that the heretofore mysterious spins producing flux noise could be O_2 molecules adsorbed on the surface. Using density functional theory calculations, we find that an O_2 molecule adsorbed on an α-alumina surface has a magnetic moment of $\sim 1.8\ \mu_B$. The spin is oriented perpendicular to the axis of the O–O bond, the barrier to spin rotations is about 10 mK. Monte Carlo simulations of ferromagnetically coupled, anisotropic XY spins on a square lattice find $1/f$ magnetization noise, consistent with flux noise in Al SQUIDs.

DOI: 10.1103/PhysRevLett.115.077002 PACS numbers: 85.25.Dq, 71.15.Mb, 73.50.Td, 74.25.Ha

Noise impairs the performance of a variety of devices based on superconducting circuits, e.g., photon detectors used in astrophysics [1], bolometers used in the search for dark matter [2], nanomechanical motion sensors [3], and quantum-limited parametric amplifiers [4]. Of particular interest are superconducting quantum interference devices (SQUIDs) [5] where low frequency $1/f$ magnetic flux noise [6] is one of the dominant sources of noise in superconducting qubits [7–10]. Experiments indicate that flux noise is produced by a high density (of order $5 \times 10^{17}\ \mathrm{m}^{-2}$) of fluctuating spins residing on the surface of normal metals [11] and superconductors [12,13], though it is independent of the materials [6]. Furthermore, experiments indicate that these spins are not independent, but rather may be clustered and have correlated fluctuations [14,15].

A number of models of flux noise have been proposed [13,16–19]. An early model of flux noise proposed that the spins are the magnetic moments of electrons in surface traps and that the spin orientation changes when an electron hops to a different trap [13]. Another model suggested that spin flips of paramagnetic dangling bonds occurred as a result of interactions with tunneling two-level systems [16]. Experimental indications of interactions between spins [12] led Faoro and Ioffe to suggest that flux noise is the result of spin diffusion via Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions [17]. RKKY interactions between randomly placed spins produce spin glasses, and Monte Carlo simulations of Ising spin glass systems show that interacting spins produce $1/f$ flux and inductance noise in agreement with experiment [18].

The microscopic origin of these spins remains unclear. Choi *et al.* [20] proposed that they are electrons in localized states at the metal-insulator interface, though spins have also been found on the surface of the dielectric, aluminum oxide, without a metal present [11]. Density functional theory (DFT) calculations [21] on sapphire (α-Al_2O_3), emulating the oxide layer that typically forms on surfaces of SQUIDs, indicate that thermodynamically stable charged vacancies are unlikely to be the source of flux noise because of the large energy differences associated with spin reorientation, though these energy differences decrease as the charge decreases. Lee *et al.* [21] used DFT to suggest that ambient molecules, such as OH, adsorbed on the surface could be the culprits, though the energy differences between different spin orientations is hundreds of degrees Kelvin, making thermal spin fluctuations unlikely.

Since SQUIDs are exposed to the atmosphere, we propose that the primary source of spins producing flux noise is O_2 molecules adsorbed on the surface. The free O_2 molecule has a spin triplet electronic configuration with a magnetic moment of $2.0\ \mu_B$ [22] and is strongly paramagnetic in its liquid phase. O_2 molecules absorbed on metal or oxide surfaces can form ordered lattices and exhibit exotic magnetic properties [23]. A natural question is whether they retain a large magnetic moment on the surface of metal oxides as well as on the surface of dielectric materials used to encapsulate SQUIDs [24]. If they do retain a large moment, it is important to know the associated magnetic anisotropy energies (MAEs) that are the energy barriers for spin reorientation and hence key to understanding thermal fluctuations. Because of the weak spin-orbit coupling of oxygen, the MAEs of these systems are small, making them difficult to investigate theoretically and experimentally.

In this Letter, using systematic DFT calculations, we report that O_2 molecules with a surface density of $1.08 \times 10^{18}\ \mathrm{m}^{-2}$ have a large magnetic moment, $1.8\ \mu_B$/molecule, on an α-Al_2O_3 (0001) surface. These spin moments are weakly coupled and can reorient almost freely in a plane perpendicular to the O–O bond, with an energy barrier at the level of a few millikelvins. Our Monte Carlo simulations on ferromagnetically coupled, anisotropic XY spins

on a 2D square lattice suggest that they indeed produce $1/f$ magnetization noise, and hence an O_2 adlayer could be responsible for the flux noise found in SQUIDs. This would explain the long standing conundrum of why flux noise does not much depend on materials [6].

Our DFT calculations were performed with the Vienna *ab initio* simulation package (VASP) [25–28], using the Perdew-Burke-Ernzerhof functional [29] for the description of the exchange and correlation interactions among electrons. We treated O-$2s2p$ and Al-$3s3p$ shells as valence states and adopted the projector-augmented wave pseudopotentials to represent the ionic cores [30,31]. The energy cutoff of the plane-wave expansion was 500 eV. The spin-orbit coupling term was treated self-consistently using the noncollinear mode of VASP [32,33], and the magnetic anisotropy energy was determined through either the torque or the total energy method [34,35]. While our main results involved α-alumina, some test calculations were also carried out for γ-alumina thin films and ultrathin alumina on a NiAl (110) surface to investigate the effects of surface roughness and complex morphology [36]. To mimic sapphire Al_2O_3 (0001) surfaces, we constructed a periodic slab model; the repeating unit consists of 18 layers of atoms and a vacuum that is 15 Å thick along the surface normal. In the lateral plane, we used a 2×2 supercell to dilute the adsorbates, corresponding to a surface density of 1.08×10^{18} m^{-2}. The lattice constant in the lateral plane was fixed according to the optimized dimensions of bulk α-Al_2O_3 ($a = b = 4.81$ Å, $c = 13.12$ Å). An $11 \times 11 \times 1$ Monkhorst-Pack [37] k-point mesh was used to sample the Brillouin zone. The criteria for structural optimization are (1) the atomic force on each atom is less than 0.01 eV/Å and (2) the energy convergence is better than 10^{-7} eV.

To describe the strength of O_2 adsorption, we define the binding energy per O_2 molecule as

$$E_b = E_{O_2/Al_2O_3(0001)} - E_{Al_2O_3(0001)} - E_{O_2}, \qquad (1)$$

where $E_{O_2/Al_2O_3(0001)}$ and $E_{Al_2O_3(0001)}$ are the total energies of the Al_2O_3 slab with and without the O_2 molecule on it. E_{O_2} is the total energy of the free O_2 molecule in its gas phase. Through studies of various initial adsorption configurations, with the O_2 molecule being placed on top of O, Al, and O–O bridge sites, we found that the most preferential absorption site for the O_2 molecule is atop the Al site on the Al_2O_3 (0001) surface, with a binding energy of −0.15 eV. This indicates that the O_2-Al_2O_3 (0001) interaction is rather weak, which is understandable since the clean Al_2O_3 (0001) surface is known to be inert towards adsorbates [38,39]. As shown by the red balls in Figs. 1(a) and 1(b), the absorbed O_2 molecule is tilted by about 55 deg away from the surface normal. The optimized O–O bond length is 1.23 Å, which is close to the experimental value 1.21 Å [40]. The nearest O-Al distance is 2.17 Å, and the Al atom underneath is pulled up by about

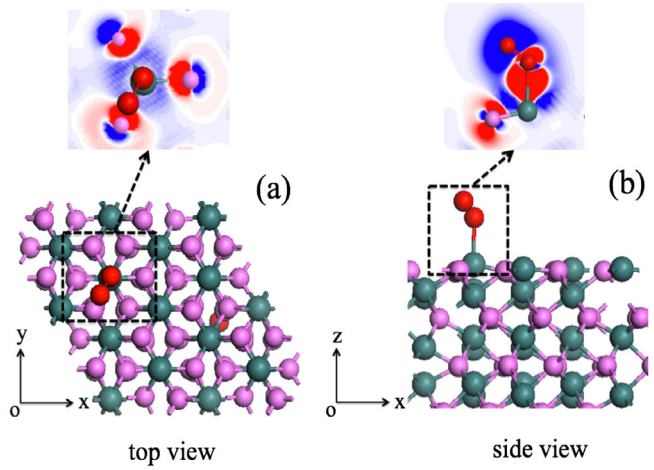

FIG. 1 (color online). Schematic atomic geometries of an O_2 molecule absorbed on an Al_2O_3 (0001) surface: (a) top view and (b) side view. The corresponding charge redistribution (the dashed rectangular area) between an adsorbed O_2 molecule and the substrate is given in the insets: red and blue represent the charge accumulation and depletion at 0.005 eV/Å^3, respectively. The red balls and green balls represent the absorbed O_2 molecule and Al atoms, respectively. The magenta balls represent oxygen atoms in the Al_2O_3 lattice.

0.34 Å from its position in the clean α-Al_2O_3(0001) surface, which is nevertheless still 0.50 Å lower than its bulklike position [41].

The total magnetic moment of each O_2 molecule on Al_2O_3 (0001) is 1.8 μ_B, slightly smaller than that in its gas phase, 2.0 μ_B. From the total density of states [peach background in Fig. 2(a)] and the projected density of states (PDOS) of the O_2 molecule [blue and green peaks in Fig. 2(a)], it is also evident that the $pp\pi^*$ orbitals of the O_2 molecule in the minority spin channel split into two separate peaks and shift down to the Fermi level from 2.0 eV for the free O_2 molecule. The small occupancy in the hybridized $pp\pi^*$ orbitals causes the charge rearrangement as depicted in the insets of Figs. 1(a) and 1(b), and is responsible for the reduction of the magnetic moment of O_2. It appears that the lower oxygen atom in O_2 and the lattice oxygen atoms gain electrons from Al and the higher oxygen atom in O_2. The spin density of the absorbed O_2 molecule in the inset in Fig. 2(a) shows a donut feature of the $pp\pi^*$ orbital, similar to that of the free O_2 molecule. Meanwhile, the underlying Al and lattice O atoms are weakly magnetized, with small spin moments of 0.01 and 0.03 μ_B, respectively.

The two key parameters for $1/f$ noise are the MAE and the exchange interaction between O_2 molecules (J_{ij}). Our DFT calculations with 2×2 and 4×4 supercells indicate O_2 molecules interact ferromagnetically on Al_2O_3 (0001), with exchange energies of 0.14 meV (~1.6 K) for two oxygen molecules 4.8 Å apart, and 0.05 meV (~0.6 K) for a separation of 9.6 Å. It appears that the substrate plays a

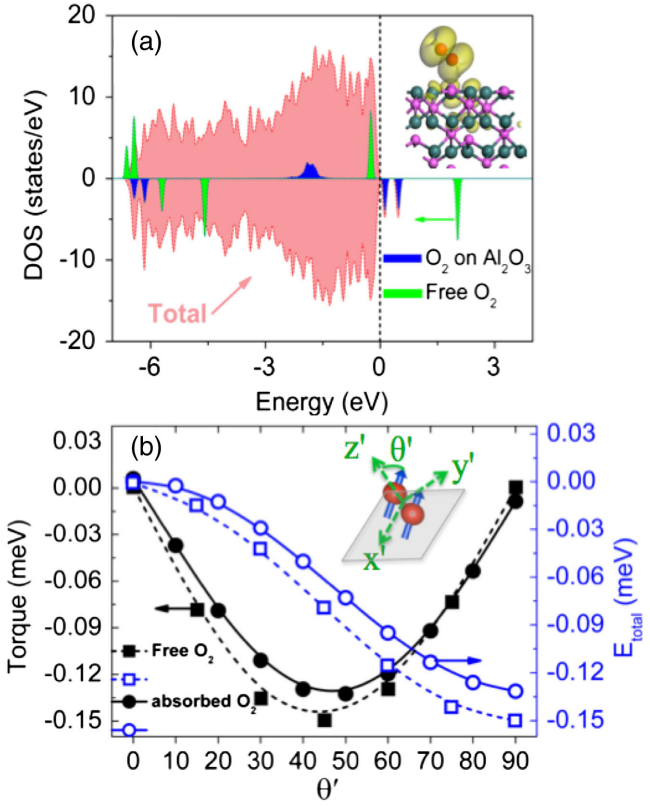

FIG. 2 (color online). (a) PDOS of the absorbed O_2 molecule on $Al_2O_3(0001)$, along with the total density of states of $O_2/Al_2O_3(0001)$ and the density of states of the free O_2 molecule. The positive and negative values correspond to states in the majority and minority spin channels, respectively. The inset gives the isosurfaces (olive) of the total spin density of $O_2/Al_2O_3(0001)$ at 0.005 $e/\text{Å}^3$. (b) Calculated torque and relative total energy (E_{total}) versus the spin orientation of the free (dashed lines) and adsorbed (solid lines) O_2 molecule. The inset defines the polar angle (θ') for the direction of the spin with respect to the z' axis that lies along the O–O bond.

key role for the magnetic coupling between O_2 molecules, because calculations for free O_2 molecules gave smaller exchange values. As seen from the PDOS curves in Fig. S1 in the Supplemental Material [42], the $pp\pi^*$ orbitals of antiferromagnetically coupled $O_2/Al_2O_3(0001)$ shift to higher energies compared to their counterparts in ferromagnetically coupled $O_2/Al_2O_3(0001)$. This indicates a slightly smaller charge gain from Al when O_2 spins are antiferromagnetically aligned compared to ferromagnetically aligned. Meanwhile, the induced spin polarization on the lattice oxygen atoms between two O_2 molecules is also somewhat suppressed in the antiferromagnetic case. These factors favor ferromagnetic coupling between O_2 molecules on $Al_2O_3(0001)$, as we will assume for the Monte Carlo simulations.

The determination of the small MAE of O_2 is still a challenge for DFT calculations. We calculated the torque $\tau(\theta')$ as a function of the polar angle θ' of the spin moment with respect to the O–O bond that lies along the z' axis as shown in the inset of Fig. 2(b): $\tau(\theta') = [\partial E_{\text{total}}(\theta')/\partial\theta'] = \sum_{\text{occ}}\psi_{i,k}|(\partial H_{\text{SO}}/\partial\theta')|\psi_{i,k}$ [34,35], in steps of 15°, as illustrated in the inset. For the *free* O_2 molecule, τ follows the function $-\sin(2\theta')$ as shown by the dashed black line in Fig. 2(b). By integrating τ from 0 to θ', we obtain the angle dependence of the total energy, $E_{\text{total}}(\theta')$. Clearly, the lowest energy corresponds to the spin aligned perpendicular to the O–O bond ($\theta' = 90°$), and the energy difference between $\theta' = 0°$ and $\theta' = 90°$ is 0.15 meV/O_2. This stems from the spin-orbit coupling interaction between the $pp\pi^*$ orbitals of O_2 in the two separate spin channels, which are depicted by two sharp green peaks at −0.2 eV (majority spin) and 2.0 eV (minority spin) in Fig. 2(a). Note that the spin rotation within the $x'y'$ plane has no energy barrier for the free O_2 molecule due to the cylindrical symmetry. Similarly, the torque associated with O_2/Al_2O_3 also follows $-\sin(2\theta')$ as shown by the solid black line in Fig. 2(b). The total energy decreases monotonically as the magnetic moment rotates away from the O–O bond towards the $x'y'$ plane and the energy difference between $\theta' = 0$ and $\theta' = 90°$ is 0.13 meV/O_2, slightly smaller than that of the free O_2 molecule. This MAE is sufficient to block the thermal spin fluctuations out of the $x'y'$ plane toward the z' axis at temperatures below 1 K. Nevertheless, spin can rotate within the $x'y'$ plane, and the corresponding energy barrier is the key to determining its contribution to magnetic noise. By using the torque and total energy methods, we found that this energy barrier is extremely small [about 1 μeV or 10 mK], almost at the limit of the precision that DFT can achieve for the determination of the MAE, so rotation of spin within the $x'y'$ plane is unblocked.

Knowing that the magnetic moments of O_2 molecules are weakly coupled on $Al_2O_3(0001)$ and can easily rotate around the O–O bond, we wanted to see if they produce the $1/f$ noise observed in SQUIDs, rather than white noise (or a Lorentzian spectrum at low temperatures), so we performed Monte Carlo simulations of classical anisotropic XY spins. We focus on exchange interactions between oxygen spins since dipolar and hyperfine [19] interaction energies are much smaller, and describe the ferromagnetic nearest-neighbor exchange interactions with the Hamiltonian

$$H = -\sum_{\langle i,j\rangle} J_{ij}(S_i^x S_j^x + S_i^y S_j^y) - A\sum_i (S_i^x)^2, \qquad (2)$$

where $S^x{}_i$ is the x component of the spin on site i *and* A is the rescaled MAE. Without loss of generality, we choose the preferred anisotropic direction to be along the x axis, which we refer to as the "easy axis." The length of the spins is 1. Since the SQUID surface is disordered and the oxygen molecules are adsorbed in random places, we choose ferromagnetic couplings $J_{ij} > 0$ from a Poisson-like distribution $P(J)$ in the following way. First, dimensionless integers C_{ij} are drawn from a Poisson distribution with a

mean of $\langle C_{ij}\rangle = 5$. Then, $J_{ij} = 0.2J_0C_{ij}$, where the average coupling $\langle J_{ij}\rangle = J_0 = 1$ sets the energy and temperature scale. For $A = 0$ and uniform coupling ($J_{ij} = 1$), we obtain the traditional 2D XY model, which undergoes a Kosterlitz-Thouless phase transition [47] at $T_C \sim 1$ (the exact value of T_C depends on the system size). We decided to use ferromagnetic couplings because (a) DFT finds ferromagnetic couplings, (b) the carrier density in the oxide is too low for spins to engage in RKKY interactions, and (c) there is experimental evidence for time reversal symmetry breaking consistent with surface spin ferromagnetism [14,18]. We performed Monte Carlo simulations with the Metropolis algorithm on a 32×32 square lattice with periodic boundary conditions. In a trial move, a site and a trial angle between 0 and 2π are randomly chosen from a uniform distribution. At each temperature, the system is allowed to equilibrate for 10^6 Monte Carlo steps per spin (MCS) before we record the time series for $M(t)$, the magnetization per spin, and for $E(t)$, the energy per spin. We then calculate the magnetization spectral density $S_M(\omega) = 2\int_{-\infty}^{\infty} dt e^{i\omega t}\langle \delta M(t)\delta M(0)\rangle$, where $\delta M(t) = [M(t) - \langle M\rangle]$. We normalize the noise power by setting the total noise power equal to σ_M^2, the variance of M: $S_{\rm tot} = (1/N_\tau)\sum_{\omega=0}^{\omega_{\rm max}} S_M(\omega) = \sigma_M^2$), where N_τ is the duration of the time series.

Our magnetization noise power results are shown in Figs. 3(a) and 3(b). At high frequencies $S_M(f) \sim 1/f^\alpha$, where the noise exponent α varies from 0.3 to 2, depending on the temperature and anisotropy. At the Kosterlitz-Thouless transition ($A = 0$ and $T = T_C \sim 1$), our exponent is consistent with the expected value of

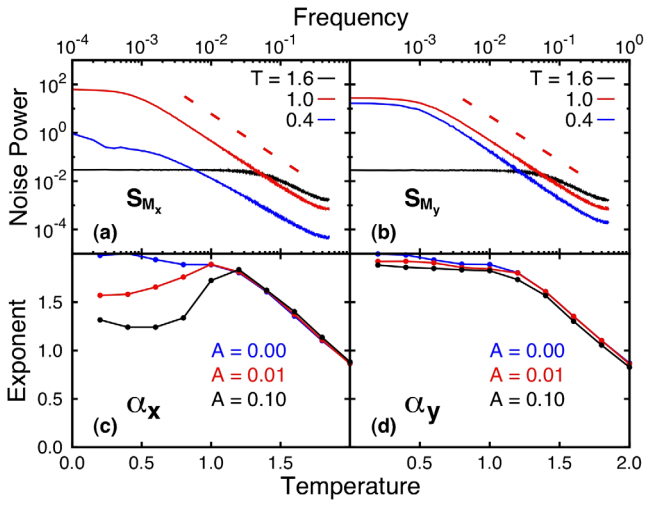

FIG. 3 (color online). (a),(b) Log-log plot of the magnetization noise power $S_M(f)$ versus frequency (in units of 0.1/MCS) for (a) M_x and (b) M_y at various temperatures for $A = 0.01$. The slopes of the dashed lines give the noise exponents α and are (a) 1.89 and (b) 1.84 for $T = 1$. The noise spectra are taken from time series with 10^7 MCS and averaged over 50 sample realizations of the couplings. (c),(d) Noise exponents versus T for various values of the anisotropy for (c) M_x and (d) M_y.

[48] $\alpha = 1 + (2 - \eta)/z \sim 1.9$ with the critical exponent $\eta = ¼$ [49] and the dynamical critical exponent $z \sim 2$ [50]. According to the actual values of J and A from the DFT calculations discussed above, the experimentally relevant parameters are $T > 1.6$ and $A \sim 0.01$. In this regime, Figs. 3(c) and 3(d) show that the noise exponents range from 1.37 (for $T = 1.6$) to 0.86 (for $T = 2.0$), which is consistent with experimental values of 0.58 to 1 [6,9]. At low frequencies the noise is white due to a finite size effect [48]. We present additional results including the specific heat and susceptibility in the Supplemental Material [42].

It is now clear that the O_2 molecules on qubits are magnetic and can produce $1/f$ noise on $Al_2O_3(0001)$. Significantly, we found that the magnetic moment of O_2 remains large and perpendicular to its bond as long as the molecule is not dissociated. Since most superconducting qubits have protective oxidized surfaces that are chemically inert, adsorbed O_2 should remain in its molecular form. For example, physisorbed O_2 molecules were found on Nb surfaces after the initial oxidation stages of the prototypical superconductor [51,52]. According to the mechanism discussed above for Al, O_2 molecules should produce magnetic flux noise in these SQUIDs as well. Indeed, similar flux noise has been experimentally studied in SQUIDs fabricated from Al, Nb, Pb, and PbIn [6,7].

While vacancies on the oxide surfaces may also produce local magnetic moments, they contribute much less to the noise since, as we show in the Supplemental Material [42], the formation energy for both Al and O vacancies is high (>2.4 eV) and hence their area density should be very low. Furthermore, none of the vacancies induces a magnetic moment on the more complex γ-alumina surface (see the Supplemental Material [42]). Our recent calculations have also found that the x-ray magnetic circular dichroism spectrum of an O_2 adlayer has a sharp feature at the onset due to the transition from the $1s$ shell to the characteristic $2\pi^*$ orbitals of O_2, very different from that of O vacancies. This offers a useful way for experimental verification in the future. The identification of O_2 adsorbates as the main source of magnetic noise has the important implication that one can reduce flux noise by protecting the surface with preoccupants such as NH_3, N_2, or CO. Our preliminary results indicate that the adsorption energy of NH_3 on sapphire is 1.8 eV per molecule, much higher than that of O_2, 0.15 eV.

In conclusion, systematic DFT calculations of $O_2/Al_2O_3(0001)$ demonstrate that the physisorbed O_2 molecule has a magnetic moment of $\sim 1.8\ \mu_B$ and a small magnetic anisotropy energy of 10 mK. Monte Carlo simulations of ferromagnetically coupled anisotropic XY spins on a square lattice find $1/f$ magnetization noise, consistent with flux noise in Al SQUIDs. We thus propose that this could be the source of low frequency flux noise in SQUIDs. Unlike vacancies, which may or may not produce magnetic moments, depending on the charge state and their local environment [21], adsorbed O_2 molecules have robust

magnetic moments because of their weak interaction with the substrate. Furthermore, the experimentally estimated density of fluctuating spins, 5×10^{17} m^{-2} [11–13], is too high for vacancies, but is reasonable for the surface density of O_2 adsorbates. Our results here imply that removing oxygen adsorbates from the surface of SQUIDs could substantially reduce flux noise.

We thank John Clarke and Robert McDermott for helpful discussions. Work at UCI was supported by DOE-BES (Grant No. DE-FG02-05ER46237) and the Army Research Office (Grant No. W911NF-10-1-0494). Work at Fudan was supported by the Chinese National Science Foundation under Grant No. 11474056. Computer simulations were performed at the U.S. Department of Energy Supercomputer Facility (NERSC).

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