

Magnetic properties of O₂ adsorbed on Cu(100): A spin-polarized metastable He beam studyM. Kurahashi,¹ X. Sun,² and Y. Yamauchi¹¹*National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan*²*University of Science and Technology of China, Hefei, Anhui 230026, China*

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Magnetic properties of O₂ adsorbed on Cu(100) were investigated by monitoring the spin dependence in Penning ionization of metastable He(2³S) under external magnetic fields of 0–5 T. A clear spin polarization was found for the 3σ_g and 1π_u orbitals of physisorbed O₂ under external fields, while the spin polarization disappeared when O₂ was changed into the chemisorbed state at >50 K. The magnetic susceptibility at the surface of multilayer and monolayer of physisorbed O₂ on Cu(100) was similar to that for the bulk liquid O₂. Observed exchange splittings and spin polarization suggest that a physisorbed O₂ molecule has a magnetic moment close to that for an isolated O₂ molecule even at submonolayer coverages, while a density functional theory calculation predicts a much reduced magnetic moment for O₂ directly adsorbed on Cu(100).

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I. INTRODUCTION

Sequential steps of physisorption, chemisorption, and dissociation of O₂ on metal and/or semiconductor surfaces have attracted much attention because of their close relation with catalytic processes, corrosion, and oxide formation. Unlike the case for other basic adsorbates, O₂ is particularly interesting because it carries electron spin derived from unpaired electrons. The spin state is important especially when characterizing a physisorbed O₂ molecule, which is bonded weakly to the surface via the van der Waals interaction and therefore is gas-phase like. Physisorbed O₂ has been identified on various metallic surfaces such as Ag,^{1–4} Pt,^{5,6} Cu,^{7,8} and Ni,⁹ and its spin state has been discussed in a number of studies.^{3–5,7} Near-edge x-ray absorption fine structure (NEXAFS) measurements of O₂ physisorbed on Pt(111) (Ref. 5) and Cu(100) (Ref. 7) clarified the exchange splittings in the oxygen 1s excitation spectra, while no such splitting was observed for the chemisorbed state. Niki *et al.*, based on the observation that the presence of physisorbed O₂ molecules largely affects the ortho-para conversion rate of H₂, suggested that physisorbed O₂ on Ag is magnetic.⁴ No electron spin resonance signal, however, has been detected for physisorbed O₂ on Ag, but this absence has been ascribed to the broadening of the resonance due to the coupling with substrate conduction electrons.³ Following these studies, physisorbed O₂ is likely to be magnetic, but there has been no experiment that directly detected the spin polarization of O₂ adsorbed on metallic substrates.

Condensed O₂ has attracted much attention also from a viewpoint of magnetism where the direct-exchange interaction and the van der Waals interaction play major roles, and the magnetic properties of bulk O₂ have been investigated in details.^{10,11} As to the magnetism of surface and thin film, O₂ films prepared on graphite have been investigated extensively.^{12–14} However, no attempts have been made to monitor the magnetic properties of O₂ on metallic surfaces, where much stronger interaction may exist between O₂ and the substrate.

In this study, we have investigated the magnetic properties of O₂ adsorbed on Cu(100) using a spin-polarized metastable helium (He*) beam, which is an extremely surface-sensitive

spin probe, under external magnetic fields of 0–5 T. By monitoring the He* spin dependence in the Penning ionization (PI), we will discuss the spin polarization of physisorbed O₂, its temperature dependence, and the magnetic susceptibility. We finally discuss the fact that physisorbed O₂ shows a definite spin polarization and exchange splittings even at submonolayer coverages, while a density functional theory (DFT) calculation predicts a much reduced magnetic moment for an O₂ molecule adsorbed on Cu(100). We will propose a nonadiabatic effect as the origin of this inconsistency.

II. EXPERIMENT

The details of the spin-polarization measurement using a He* beam under high external magnetic fields have been described elsewhere.^{15–17} In brief, a spin-polarized He*(2³S) beam impacts the surface along the surface normal, and the He* spin dependence in the yield of electrons ejected via the He* deexcitation on the surface was monitored by measuring the sample compensation current under external magnetic fields applied perpendicularly to the surface.^{15–17} The magnitude of the applied magnetic fields will be indicated in each experimental result. The He* spin dependence in the PI will be discussed in terms of the spin asymmetry *A* defined by

$$A(V_S) = \frac{I_{\uparrow}(V_S) - I_{\downarrow}(V_S)}{I_{\uparrow}(V_S) + I_{\downarrow}(V_S)}, \quad (1)$$

where *I*_↑(*V*_{*S*}) [*I*_↓(*V*_{*S*})] is the sample current for the He* spin magnetic moment parallel (antiparallel) to the magnetic field at the sample voltage of *V*_{*S*}. Since the ejected electrons with the kinetic energy ≥ *eV*_{*S*} contribute to *I*(*V*_{*S*}), we can discuss the spin polarization of the PI peaks by measuring the *V*_{*S*} dependence in *I*_↑ and *I*_↓. We also conducted metastable deexcitation spectroscopy (MDS) measurements with a retarding field analyzer under no applied magnetic field.¹⁷ When conducting the MDS measurement, the residual magnetic field at the sample position was compensated for by three pairs of Helmholtz coils. A Cu(100) surface was prepared by repeating cycles of annealing at 973 K and 1 kV Ne⁺ sputtering. The surface cleanliness and crystallographic order were monitored with Auger electron spectroscopy and low-energy electron diffraction. After cleaning the surface, the Cu(100) substrate

was transferred to the analysis chamber and cooled to 18–20 K by means of a He-flow cryostat. The sample temperature was measured with a Chromel-AuFe thermocouple attached to the sample holder. O₂ was dosed onto the Cu surface by backfilling the chamber with O₂ gas using a variable leak valve. The base pressure of the analysis chamber was $<1 \times 10^{-8}$ Pa.

III. MDS SPECTRA AND HE* DEEXCITATION

Figure 1 shows the MDS spectra measured at various O₂ exposures at 18 K. The MDS spectrum of the Cu clean surface shows broad and structureless features, which are caused by resonance ionization (RI) followed by Auger neutralization (AN) of He*.¹⁸ By adsorbing O₂, photoemission-like features associated with the PI, in which a surface electron fills the He* 1s hole with simultaneous emission of the He* 2s electron, appear. The PI peaks start to grow steeply from ~ 5 L and tend to saturate at >15 L as can be seen also in the change of the total electron yield (Fig. 2). This indicates that the multilayer starts to grow from ~ 5 L and covers the whole surface at ~ 15 L. Similar behaviors have been reported for metallic surfaces covered with various molecular adsorbates,^{8,19} and the slope change in the electron yield can be associated with the completion of the monolayer and the onset of multilayer island growth.¹⁹ The electron yield is higher on the multilayer surface because He* decays mainly via the PI, which causes an electron yield higher than that for the RI + AN, while the RI + AN also occurs on monolayer surface.

The origin of the PI peaks observed for the O₂ multilayer surface^{8,9} has been discussed on the basis of the PI of gas phase O₂.^{20,21} Peaks A, B, and C have been assigned to the PI to the $^2\Sigma_g^-$, $^4\Sigma_g^-$, and $^4\Pi_u$ states of an O₂⁺ ion, respectively.^{8,9} To discuss the spin dependence in the PI peaks, we computed the spin-resolved local density of states (LDOS) for an isolated O₂ molecule [Fig. 3(a)] and for the surface of α -O₂

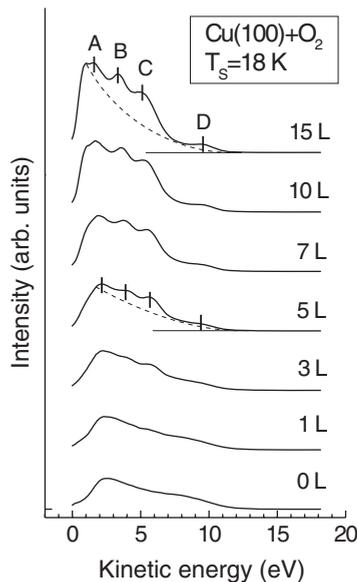


FIG. 1. Metastable deexcitation spectra of Cu(100) at O₂ exposures are shown. The dashed line corresponds to the background assumed for the secondary electrons and ionic decay channel of (2).

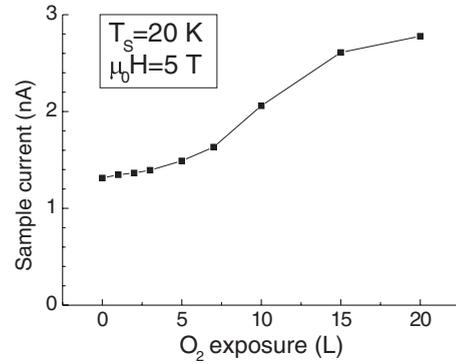


FIG. 2. The yield of electrons ejected by He* at various O₂ exposures. The measurements were conducted at $\mu_0 H = 5$ T.

[Fig. 3(b)] using the Vienna *ab initio* simulation program.²² The surface was represented by a five-layer slab with a vacuum region of 1.38 nm. The projector-augmented wave method for the electron-ion interaction and the generalized gradient approximation (GGA) for the exchange-correlation functional were used with an energy cutoff of 400 eV. Eight *p* electrons of O₂ occupy the $3\sigma_g$, $1\pi_u$, and $1\pi_g$ orbitals, and the two $1\pi_g(\uparrow)$ electrons induce exchange splittings in the $3\sigma_g$ and $1\pi_u$ orbitals. The LDOS for the surface of α -O₂ shows a broader peak width due to the overlap between the neighboring O₂ molecules. However, because α -O₂ is the lowest temperature phase and has the shortest intermolecular distance, high-temperature phases having longer intermolecular distances should have narrower LDOS peaks. Since the LDOS peaks of condensed O₂ are well separated with each other, the PI peaks can be discussed based on the LDOS for an isolated O₂ molecule.

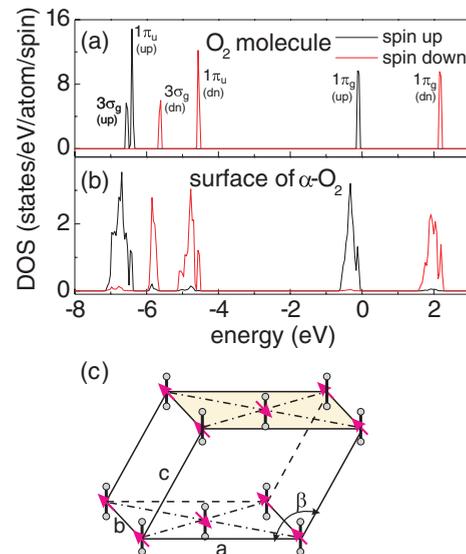
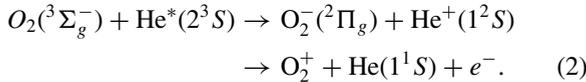


FIG. 3. (Color online) The computed local density of states of oxygen in (a) an isolated O₂ molecule and (b) at the surface of α -O₂. The surface structure of α -O₂ is shown in (c). The Fermi energy was set to the position of the highest occupied molecular orbital. The experimental interatomic distance and the bulk lattice parameters have been used for the calculations.

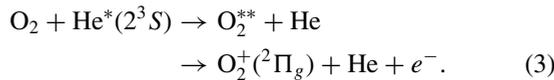
The three PI peaks (A–C) can be associated with the calculated LDOS for an isolated O₂ molecule. The $1\pi_u(\uparrow)$ and $3\sigma_g(\uparrow)$ states, because of their close energies, would contribute to peak A. Peaks B and C can be associated with the $3\sigma_g(\downarrow)$ and $1\pi_u(\downarrow)$ states, respectively. In the PI process, the spin of the electron that fills the He* 1s hole must be opposite to the He* spin. Therefore, peak A is due to He* having spin antiparallel to O₂, while peaks B and C are due to the parallel configuration.

When discussing the spin asymmetry for the PI peaks, we also have to consider the contribution of the inelastically scattered secondary electrons and the following ionic decay channel^{8,9,20,21} as the origin of slowly decreasing background:



The initial charge exchange process proceeds when $\text{O}_2(^3\Sigma_g^-) + \text{He}^*(2^3S)$ forms singlet or triplet while this process is prohibited for the parallel spin configuration.^{20,21}

Peak D has been attributed not to the Penning ionization, but to the following excitation energy transfer and the subsequent autoionization²⁰:



Considering the efficiency of the energy transfer, Leisin *et al.* have ascribed O₂** to a Rydberg state having an energy close to He*(2³S) (19.8 eV).²⁰ Since O₂** is triplet, the initial state [He*(2³S)+O₂(³Σ_g⁻)] must form a triplet, too.²⁰ Following this assignment, this energy transfer process does not proceed when He* and O₂ have parallel or antiparallel spin configurations. No spin asymmetry is therefore expected to appear for this process when magnetizing O₂.

IV. SPIN POLARIZATION OF PHYSISORBED O₂ MOLECULES

A. Spin dependence in the Penning ionization

Figure 4 shows the spin asymmetry in the sample current measured at $\mu_0 H = 5$ T as a function of the sample voltage. $A(V_S) = 0$ at 0 L reflecting the nonmagnetic nature of the clean Cu surface. The asymmetry increases almost linearly with the

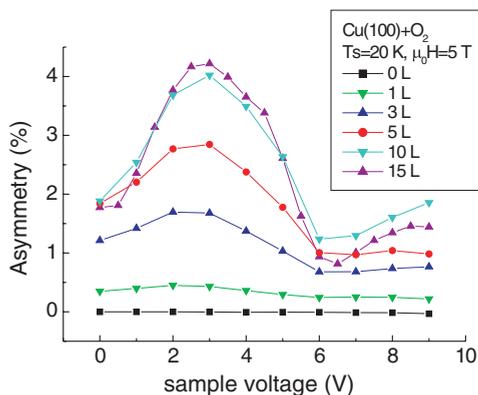


FIG. 4. (Color online) The sample voltage dependence in the spin asymmetry measured at $\mu_0 H = 5$ T and at the O₂ exposures shown.

O₂ exposure until the monolayer coverage (5 L) and tends to saturate at around 15 L, at which the multilayer covers the whole Cu surface. In addition, the shape of the $A(V_S)$ curve at submonolayer coverages resembles that for the multilayer surface at the energy range of $V_S < 6$ V. This indicates that, even at submonolayer coverages, the physisorbed O₂ molecules have nonzero magnetic moments and that the exchange splitting of the molecular orbitals corresponding to peaks A–C is similar to that for the O₂ multilayer surface. It has been reported that O₂ dissociation is happening on Cu(100) even at 4 K (Ref. 23) when the O₂ coverage is < 0.1 monolayers. However, if the dissociation is dominant at low coverages, the asymmetry should not increase linearly with the O₂ exposure since the dissociated species would be nonmagnetic. Our results therefore indicate that the molecular oxygen is the dominant adsorbate even at < 1 L and at 20 K.

The asymmetry is positive and shows a maximum at around $V_S = 3$ V. This is consistent with the He* spin dependence in the PI corresponding to peaks A–C. Under an external magnetic field (H), O₂ molecules with their magnetic moments parallel to H become dominant. The asymmetry defined by Eq. (1) is therefore positive (negative) for the PI that occurs when the magnetic moments of O₂ and He* are parallel (antiparallel) to each other. As noted in Sec. III, peaks B and C occur in the parallel configuration, while peak A does in the antiparallel configuration. The positive asymmetry is therefore expected at $V_S > 3$ V where peaks B and C make a dominant contribution to the sample current. The asymmetry is, however, expected to become lower at $V_S < 3$ V because of the contribution of peak A. The ionic decay channel of (2), which occurs in the antiparallel configuration, may decrease the asymmetry, but its contribution would be much less since Fig. 4 shows the positive asymmetry over all V_S ranges.

The origin of the positive asymmetry at $V_S > 6$ V observed for the multilayer surface is not clear. As discussed in the previous section, no field dependence is expected in the spin asymmetry for the process of (3). If there is a small contribution of PI involving the $1\pi_g$ state, the asymmetry should be negative because the $1\pi_g$ orbital has only spin-up electrons. It is also noted that the positive asymmetry at $V_S > 6$ V is observed also at submonolayer coverages. This will be discussed in Sec. IV D.

B. Temperature dependence of the spin polarization

Figures 5(a) and 5(b) show the variation of the spin asymmetry and the sample current, respectively, when warming the O₂ multilayer on Cu(100) from 20 to 60 K. Figure 5(b) indicates that the sample current is nearly constant until 30 K, but it decreases steeply at around 30 K. This can be associated with the desorption of the multilayer, which has been shown to occur at around 25 K by thermal desorption spectroscopy (TDS).⁷ It has been shown that the O₂ multilayer changes to the physisorbed monolayer at this temperature.⁷ The large decrease of the sample current is due to the difference in the electron yield between the multilayer and the monolayer noted in Sec. III. Note that the asymmetry remains even when the multilayer changes to the physisorbed monolayer at 30–40 K [see Fig. 5(a)]. This again indicates that the physisorbed molecules keep their spin polarization

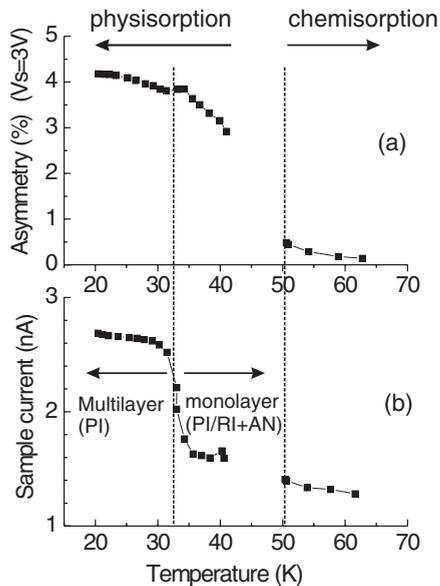


FIG. 5. The change in (a) the spin asymmetry and (b) the sample current at $\mu_0 H = 5$ T when warming the Cu(100) surface exposed to 20 L of O_2 at 18 K. The sample current was unable to measure correctly at 40–50 K because of the O_2 desorption.

even at the monolayer coverage. Figure 5(a) shows that the asymmetry strongly decays at >50 K, indicating the adsorbed O_2 molecules become nonmagnetic at >50 K. This is consistent with the previous TDS and NEXAFS study⁷ showing that the adsorption state changes from physisorption to chemisorption at 40–50 K and that chemisorbed O_2 has no exchange splittings.

The asymmetry that remains at >50 K would originate mainly from the physisorbed molecules remaining on the surface. Previous TDS study⁷ shows a broad peak corresponding to the physisorbed monolayer at 35–70 K, indicating that physisorbed O_2 still exists even at >50 K when warming the physisorption layer prepared at lower temperatures. We also note that the asymmetry at 35–40 K decreases considerably with temperature, while the temperature dependence is weaker at <30 K. This might come also from the broad TDS peak⁷ for the physisorbed monolayer. The desorption of the physisorbed O_2 and/or its transformation to the nonmagnetic chemisorbed states are happening already at 35 K, and the density of the magnetic physisorbed molecule decreases with temperature, causing the decrease in the asymmetry at 35–40 K. In contrast, the desorption of the multilayer, even if it happens at <30 K, would have a little effect on the asymmetry because the multilayer and physisorbed monolayer have similar spin polarizations (Fig. 4).

C. Magnetic susceptibility of physisorbed O_2

Figure 6 shows the magnetic field dependence in $A(V_S = 3$ V) measured at the multilayer coverage. Similar to the results of the susceptibility measurements reported for bulk O_2 (Refs. 10 and 11) and O_2 films on graphite,¹³ the asymmetry increases linearly with H . This indicates the paramagnetic or antiferromagnetic nature of O_2 physisorbed on Cu(100).

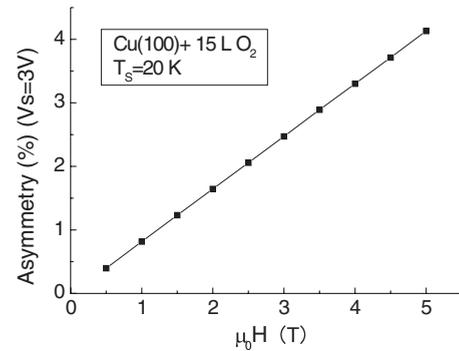


FIG. 6. The magnetic field dependence of the spin asymmetry measured at the sample voltage of 3 V and at an O_2 exposure of 15 L.

The susceptibility of physisorbed O_2 can be estimated as follows. Peaks B and C are associated with the PI of the $3\sigma_g(\downarrow)$ and $1\pi_u(\downarrow)$ orbitals which are nearly -100% polarized when the O_2 spins are completely aligned. If peaks B and C are purely due to the PI and their spin asymmetry is α , the surface magnetization is equal to $M_0\alpha$, where M_0 is the O_2 magnetic moment at the multilayer surface. Since an O_2 molecule at the multilayer surface is well separated from the Cu substrate, its magnetic moment can be approximated to be that for an isolated O_2 molecule ($2\mu_B$). The electron yield corresponding to the energy window containing peaks B and C is obtained from $I(V_S = 3$ V)– $I(V_S = 6$ V), and the corresponding spin asymmetry derived from the $I(V_S)$ curve measured at 5 T is 4.6%. We here need to consider that peaks B and C are overlapped with a slowly decreasing background shown with a dashed line in Fig. 1. If we assume the background contribution of $60\pm 10\%$ considering its uncertainty and no He^* spin dependence in its intensity, we can estimate the magnetic susceptibility $\chi = 800 \pm 200 \times 10^{-6}$ (emu/g).²⁴ This would be an underestimate because the ionic decay channel of (2), which contributes to the background, would cause a negative asymmetry.

The susceptibility at the monolayer coverage can be estimated similarly. The spin asymmetry of peaks B and C obtained similarly is 3.3% at 5 L. Since the separation of peaks A–C, which reflects the magnitude of the exchange splitting, and the shape of the $A(V_S)$ curves measured at submonolayer coverages are similar to those for the multilayer surface (see Figs. 1 and 4), it may be reasonable to assume that the magnetic moment at the monolayer coverage would also be close to that of an isolated O_2 molecule. This is consistent with the NEXAFS spectra showing the similar exchange splitting for the multilayer and the monolayer of O_2 on Cu(100).⁷ The MDS spectrum at 5 L is also overlapped with the slowly decreasing background (Fig. 1). If we assume the O_2 magnetic moment of $2\mu_B$ and the background contribution of $65\pm 10\%$, χ can be estimated to be $700 \pm 200 \times 10^{-6}$ (emu/g), which is similar to the susceptibility for the multilayer surface. This similarity can also be found from the temperature dependence data of Fig. 5(a), showing comparable asymmetries for surfaces of the O_2 multilayer and the physisorbed monolayer.

The estimated susceptibilities are now compared with those for bulk O_2 and physisorbed O_2 on graphite. The susceptibility (χ) has been reported to be 50×10^{-6} (emu/g) at 20 K

for the bulk α phase.^{10,11} χ for the liquid O₂ is 300×10^{-6} (emu/g) at 54 K,^{10,11} and its value extrapolated with the Curie law for paramagnetism should be around 800×10^{-6} (emu/g) at 20 K. Murakami *et al.*¹³ have reported that the susceptibility for the monolayer O₂ on graphite is 110×10^{-6} (emu/g) for the ζ phase at 20 K and 400×10^{-6} (emu/g) for the fluid phase at 40 K.²⁵ The smaller χ values at the low-temperature bulk α phase¹¹ and the ζ phase on graphite¹³ have been associated with the presence of the long-range antiferromagnetic ordering, and the large- χ values at high-temperature phases are due to the absence of such long-range magnetic ordering. The fact that the susceptibility estimated for the physisorbed O₂ molecules on Cu(100) is similar to that for the liquid O₂ or the fluid phase of O₂ films on graphite may therefore indicate the absence of the long-range magnetic ordering in the O₂ physisorption layer on Cu(100) at 20 K. We note that, although the susceptibility of bulk O₂ increases largely with temperature at 20–50 K,^{10,11} the susceptibility of the O₂ multilayer surface is similar to that of the monolayer phase at 35–40 K [Fig. 5(a)]. This supports the conclusion that the O₂ multilayer surface is paramagnetic even at 20 K.

The large- χ value for the O₂ monolayer on Cu(100) might be related to its surface structure. It has been reported that the O₂ monolayers on graphite¹⁴ and Ag(111) (Ref. 1) form ordered structures incommensurate with the substrate. This would be because the O₂-O₂ interaction, which is due to the van der Waals and magnetic exchange forces, is stronger than the O₂-substrate interaction. However, since Cu is more reactive than graphite and Ag, O₂ may be bonded more strongly with the substrate. Actually, the previous structural analysis with surface EXAFS (Ref. 7) has employed a model in which a physisorbed O₂ molecule is located on the fourfold hollow site. The nearest-neighbor (NN) and second-NN distances between the hollow sites are 0.255 and 0.361 nm, respectively, while the NN intermolecular distances in bulk α phase and ζ phase on graphite are about 0.32 nm.¹³ Considering the repulsion between O₂ molecules, the closest distance possible for O₂ molecules adsorbed on the Cu(100) hollow sites would be 0.361 nm. Since this distance is considerably longer than at these two O₂ phases, the magnetic interaction between physisorbed O₂ molecules would be much weaker, possibly causing a larger χ .

As to the susceptibility for the multilayer, Murakami *et al.* have pointed out the difference in magnetism between the first and second layers of the O₂ bilayer on graphite.¹³ The long-range magnetic ordering is missing in the second layer because the second layer, which is incommensurate with the first layer, may feel random exchange fields from the first layer.¹³ This effect is likely to exist also in the present case. Since He* monitors the outermost surface of the O₂ multilayer, the susceptibility estimated above reflects the magnetic properties of the multilayer surface, which is more disordered magnetically than the inner layers. This might be one of the origins of the observed large susceptibility.

D. Comparison with the electronic states computed for O₂ adsorbed on Cu(100)

To further discuss the spin state of physisorbed O₂, we conducted DFT calculations for O₂ adsorbed on Cu(100). O₂

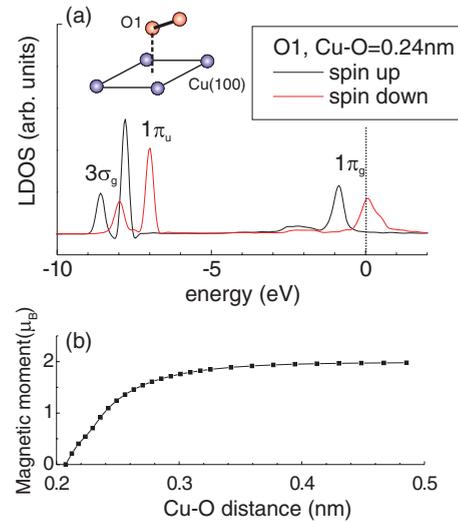


FIG. 7. (Color online) (a) The local density of states computed for the oxygen atom (O1) in an O₂ molecule adsorbed on Cu(100). The nearest-neighbor Cu-O distance was set to be 0.24 nm. (b) The variation of the magnetic moment of O₂ as a function of the Cu-O distance. The O-O distance was set to be 0.123 nm for all of the Cu-O distances shown.

was adsorbed on a 2×2 surface represented by a five-layer slab with a vacuum spacing of 1.8 nm. Following the previous surface EXAFS experiment,⁷ one end of the O₂ molecule is adsorbed on the fourfold hollow site of an unrelaxed Cu(100) with its axis tilted 23° from the surface. Figure 7(a) shows the LDOS of oxygen computed with the NN Cu-O distance of 0.24 nm. The NN distance has been determined to be 0.207 nm by the surface EXAFS analysis,⁷ but our calculation, as shown in Fig. 7(b), indicates that O₂ loses its magnetic moment completely at this distance. It is shown that, even at the Cu-O distance of 0.24 nm, the exchange splitting of the $1\pi_u$ orbital decreases to half of the isolated O₂ case [see Fig. 3(a)]. Figure 7(b) plots the magnetic moment of O₂ as a function of the Cu-O distance. Here, the magnetic moment was derived from the difference between the spin-up and spin-down charges integrated above the Cu surface. The computed magnetic moment decreases gradually with decreasing the distance and quenches completely at around 0.21 nm.

Our experiments and the previous NEXAFS result,⁷ however, have indicated that physisorbed O₂ at submonolayer coverages shows exchange splittings similar to the O₂ multilayer and therefore seems to have a magnetic moment close to that of an isolated molecule. In addition, if the exchange splitting of the $1\pi_u$ orbital decreases as shown in Fig. 7(a), the $A(V_S)$ curve of Fig. 4 should show a large coverage dependence at around 3–4 V, where the $1\pi_u(\uparrow)$ orbital should contribute largely at submonolayer coverages. The $A(V_S)$ curve for submonolayer coverages, however, resembles that for the multilayer coverage at $V_S < 6$ V, indicating no coverage dependence in the exchange splittings. This is surprising considering our calculation showing no magnetization at the Cu-O distance determined experimentally.⁷

There are two possible origins for this discrepancy. One is that the Cu-O distance determined experimentally⁷ seems to be too short. [Considering the NN intermolecular distance in

α -O₂ (0.32 nm, Ref. 10) and the Cu atomic radius (0.13 nm), the reasonable Cu-O distance for the van der Waals bonding might be ~ 0.29 nm. To resolve the discrepancy between this simple estimation and the previous surface EXAFS analysis,⁷ additional structural analysis that can determine the Cu-O distance for physisorbed O₂ would be necessary.] The other is the problem of the adiabatic calculation. The importance of the nonadiabatic effect has been discussed for the O₂ dissociation on Al(111).^{26,27} It has been shown that an adiabatic calculation causes the partial quenching of the O₂ spin, which occurs even at large O₂-surface distances, and results in barrierless pathways inconsistent with the low initial sticking probability (S_0) of O₂ on Al(111).^{26,27} The translational energy dependence of S_0 was explained by assuming that O₂ follows the diabatic spin-triplet curve, in which the spin is constrained around the O₂ molecule, until the spin transition occurs.^{26,27} If this is true also on a Cu surface, the following situation is expected. An O₂ molecule approaching the surface should be in the triplet state at least until the position where the triplet and singlet potential energy curves cross each other. The crossing point is located at the O-surface distance of ~ 0.25 nm for O₂/Al(111),²⁶ and is expected to be at a similar distance for O₂/Cu considering the similar atomic radius of Al and Cu. If the O₂ molecule gets trapped into the physisorbed state before reaching the crossing point, the physisorbed O₂ should be in the triplet state and therefore keep the magnetic moment of an isolated O₂ perfectly. This is consistent with the observed exchange splittings of O₂ physisorbed on Cu(100).

The spin-constrained calculation of O₂ on Al(111) shows that the triplet spin localized in O₂ causes the surrounding region of the metal surface to have a high spin-down density.²⁷ If this occurs also in O₂/Cu(100), the positive A_S at $V_S > 6$ V observed at submonolayer coverages might be explained as follows. When He* interacts with the conduction electrons, to which the physisorbed triplet O₂ molecules induce high spin-down densities, the dominant He* decay channel is the AN in which the spin-down electron neutralizes He⁺(\uparrow). This AN channel is dominant when the spins of O₂ and He* are parallel to each other, causing the positive A_S .

V. CONCLUSION

By monitoring the He* spin dependence in the Penning ionization under high magnetic field, we have observed the spin polarization in the molecular orbitals of O₂ physisorbed on metallic surface. It has been found that O₂ physisorbed on Cu(100) has a large susceptibility comparable with that of the bulk liquid O₂, suggesting the absence of the long-range antiferromagnetic ordering in the O₂ physisorption layer. We have suggested that physisorbed O₂ molecules might keep the magnetic moment of an isolated molecule because of the nonadiabatic effect.

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