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Large Inverse Tunnel Magnetoresistance in Magnetic Tunnel Junctions with an Fe₃O₄ Electrode

Shoma Yasui,¹ Syuta Honda^{1,2}, Jun Okabayashi,³ Takashi Yanase,⁴
Toshihiro Shimada,⁴ and Taro Nagahama^{4,*}

¹*Graduate School of Chemical Sciences and Engineering, Hokkaido University, Sapporo, Hokkaido 060-8628, Japan*

²*Pure and Applied Physics, Kansai University, Suita, Osaka 564-8680, Japan*

³*Research Center for Spectrochemistry, The University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan*

⁴*Graduate School of Engineering, Hokkaido University, Sapporo, Hokkaido 060-8628, Japan*

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Spinel-type magnetite Fe₃O₄ is predicted to be a half-metal material with negative spin polarization. However, magnetic tunnel junctions (MTJs) using an Fe₃O₄ electrode exhibit a small tunnel magnetoresistance (TMR) effect, the sign of which has not been established experimentally. The development of Fe₃O₄ as an excellent TMR material requires a better understanding of the characteristics of the interface and the phase transition of Fe₃O₄ called the Verwey transition. We fabricate MTJs using epitaxial Fe₃O₄-based stacks on MgO(001) substrates and find a large inverse TMR ratio of −55.8% at 80 K, which corresponds to 126% by the optimistic definition of the TMR ratio. The temperature dependence of the TMR ratio is significantly affected by the Verwey transition. Moreover, we investigate the dependence of TMR on oxygen partial pressure during Fe₃O₄ deposition. It is found that the magneto-transport properties of the MTJs show different behaviors depending on the oxygen partial pressure because the Verwey transition is sensitive to the oxygen concentration. Furthermore, the electronic and magnetic properties at the interfacial regions are investigated by x-ray magnetic spectroscopy and first-principles calculation. These findings greatly support the use of Fe₃O₄ in spintronic devices and should lead to further developments in oxide spintronics.

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I. INTRODUCTION

Since magnetite Fe₃O₄ exhibits ferrimagnetic and conductive properties at room temperature, numerical studies have been conducted using Fe₃O₄ as a spintronic material [1–3]. In particular, it was predicted theoretically to have electronic states corresponding to a half-metal with perfect negative polarization of −100% at the Fermi level [4,5], thereby creating a large tunnel magnetoresistance (TMR) effect, which is a key technology in spintronics [6]. Therefore, many researchers have worked to create large TMR in magnetic tunnel junctions (MTJs) employing Fe₃O₄. However, this has not yet been successful because of the difficulty of forming an abrupt interface between the Fe₃O₄ and insulating barriers [2,7–14]. Moreover, even the sign of the TMR depends on the growth conditions. The reasons behind these unexpected tunneling characteristics have not been clarified, and it remains an open question as to whether Fe₃O₄ acts as a high-functional material in MTJs.

The half-metallicity of Fe₃O₄ has been investigated theoretically and experimentally. Yanase and Shiratori pointed out that only majority spin electrons have a gap at the Fermi level in Fe₃O₄ [4], and many theoretical studies involving *ab initio* calculations have confirmed this [5,15,16]. The spin polarization of Fe₃O₄ was estimated by spectroscopic experiments to be −80% and −60% for the (111) and (100) surfaces, respectively [15,17–19]. These results clearly indicate that Fe₃O₄ has a high spin polarization. In contrast, the TMR ratio in Fe₃O₄ MTJs has remained low. Suzuki *et al.* investigated a number of Fe₃O₄ MTJs using an La_{1−x}Sr_xMnO₃ electrode [20–25] and observed a TMR of −33% in a high magnetic field of 7 T [25]. Kado observed variation in the TMR ratio from −28% to +30% and found a correlation between the sign of the TMR and the junction resistance in Fe₃O₄/MgO [7]. Marnitz *et al.* argued that Mg migration from a MgO barrier could change the sign of TMR [8]. In a previous study, we obtained an inverse TMR effect of −15% in a MTJ using Fe₃O₄(110) electrodes [14], and also observed phenomena like the inverse tunnel magnetocapacitance effect [26].

*nagahama@eng.hokudai.ac.jp

The important factors for enhancing the TMR effect are as follows: (1) utilizing a counter electrode with high spin polarization and (2) optimizing the crystallinity at the Fe_3O_4 /barrier interface. In this paper, we fabricate fully epitaxial MTJs of $\text{Fe}_3\text{O}_4(001)/\text{MgO}(001)/\text{Fe}(001)$ and succeed in observing a large inverse TMR effect of -55.8% at 80 K, which exceeds 100% when we adopt an optimistic definition of the inverse TMR ratio. We find that the TMR ratio strongly depends on the partial oxygen pressure during the Fe_3O_4 deposition. Furthermore, in order to clarify the microscopic mechanism, we employ element-specific x-ray magnetic spectroscopy and band-structure calculations. We discuss the relation between TMR and electronic structures.

II. EXPERIMENTS

Multilayers are prepared by molecular beam epitaxy in a chamber at a base pressure of 10^{-8} Pa. The layer structure of the MTJs is $\text{MgO}(100)/\text{buffer-MgO}(20\text{ nm})/\text{NiO}(5\text{ nm})/\text{Fe}_3\text{O}_4(60\text{ nm})/\text{MgO}(2.5\text{ nm})/\text{Fe}(10\text{ nm})/\text{Au}(30\text{ nm})$. The 20-nm MgO buffer layer is grown at a substrate temperature (T_{sub}) of 673 K on the $\text{MgO}(100)$ substrate that is prebaked at 1073 K. The NiO layer is deposited at 573 K to prevent the diffusion of Mg from the buffer layer and substrate. The Fe_3O_4 layer is grown by reactive deposition at T_{sub} of 573 K under an O_2 atmosphere. We prepare Fe_3O_4 layers at different oxygen partial pressures of 4×10^{-4} , 1×10^{-4} , and 5×10^{-5} Pa for Samples 1, 2, and 3, respectively. The Fe_3O_4 layers are then annealed at 873 K for 30 min in an O_2 atmosphere at 1×10^{-4} Pa. The MgO barrier layer is formed by evaporation of single-crystal MgO at room temperature followed by annealing at 423 K for 30 min. The 10-nm-thick Fe layer and Au cap layer are deposited at room temperature.

The crystallinity and epitaxial growth of the films are monitored by reflection high-energy electron diffraction (RHEED) and x-ray diffraction (XRD). After the growth of the multilayered stacks, MTJ structures with a junction area of $10 \times 10\text{ }\mu\text{m}^2$ are patterned by a conventional microfabrication process with photolithography and Ar ion milling. The current-voltage (I - V) characteristics and magnetoresistance are measured by the dc four-probe method. X-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) are performed at BL-7A in Photon Factory at the High Energy Accelerator Research Organization (KEK). A magnetic field of ± 1 T is applied along the incident polarized soft-x-ray beams, with the circularly polarized absorption signals defined as μ^+ and μ^- . The XAS and XMCD are defined by $(\mu^+ + \mu^-)/2$ and $\mu^+ - \mu^-$, respectively. The total electron yield mode is adopted. All XAS and XMCD measurements are carried out at room temperature.

III. RESULTS AND DISCUSSION

The epitaxial growth and crystal structure are confirmed by XRD and RHEED. The lattice constants in bulk are 4.21 Å for MgO (a_{MgO}), 8.396 Å for Fe_3O_4 ($a_{\text{Fe}_3\text{O}_4}$), and 2.87 Å for Fe (a_{Fe}) (4.073 Å for $\sqrt{2}a_{\text{Fe}}$). A clear streak RHEED pattern is observed for the Fe_3O_4 layer as shown in Fig. 1(a), indicating the formation of a film with a flat surface. Furthermore, a characteristic $\sqrt{2} \times \sqrt{2}$ R45 superlattice peak is also observed on the $\text{Fe}_3\text{O}_4(001)$ surface [27]. The surfaces of MgO also show a clear streak pattern as shown in Fig. 1(b). This confirms that the MTJ consists of layer-by-layer epitaxial growth. For Fig. 1(c), the RHEED pattern is slightly spotty, meaning epitaxial growth with a roughness of 2 nm in the surface [an Atomic Force Microscope (AFM) image of Fe surface is shown in Fig. S1 in the Supplemental Material [28]]. We also perform TEM observation to obtain a cross-section image of MTJs and then atomically flat interfaces are confirmed (see Fig. S2 in the Supplemental Material [28]).

In the XRD profile for the $\text{Fe}_3\text{O}_4/\text{MgO}/\text{Fe}$ film in Fig. 1(d), only the (004) and (008) peaks are found for Fe_3O_4 , which is consistent with the RHEED results. The XRD peaks of $\text{Fe}_3\text{O}_4(004)$ and $\text{MgO}(002)$ are nearly the same at 42.98° and 43.30° , respectively. The lattice constant for the c axis of Fe_3O_4 is 8.369 Å, which corresponds to a difference of 0.32% from the bulk value of 8.396 Å. This results in a very small lattice mismatch with MgO of 0.29%. The $\text{Fe}(002)$ peak is also observed because of epitaxial growth of the upper electrode.

The TMR effect of Sample 1 deposited at 4×10^{-4} Pa is shown in Fig. 2(a). The TMR is -9.6% at room temperature and -55.8% at 80 K. The obtained inverse TMR indicates that the polarization of Fe_3O_4 ($P_{\text{Fe}_3\text{O}_4/\text{MgO}}$) is negative, which is consistent with the band calculations.

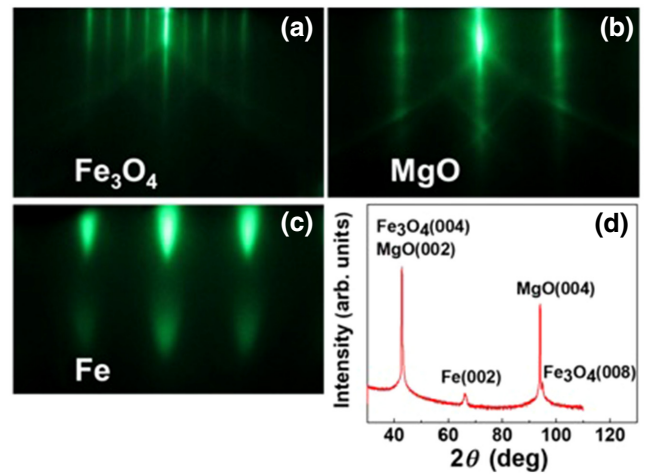


FIG. 1. RHEED patterns for each layer: (a) Fe_3O_4 , (b) MgO, and (c) Fe. (d) XRD profile for $\text{MgO}(001)/\text{Fe}_3\text{O}_4(001)/\text{MgO}(001)/\text{Fe}(001)$.

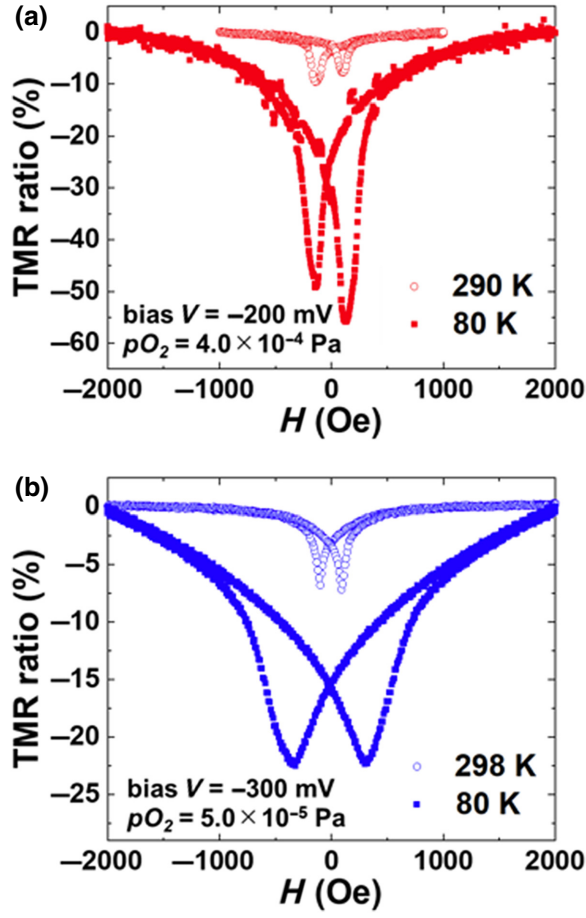


FIG. 2. TMR curves for $\text{Fe}_3\text{O}_4(001)/\text{MgO}(001)/\text{Fe}(001)$ MTJs deposited in an oxygen atmosphere at (a) 4×10^{-4} Pa (Sample 1) and (b) 5×10^{-5} Pa (Sample 3). The TMR curves are measured at room temperature and 80 K.

With respect to the spin polarization, the polarization at 80 K is estimated to be $P_{\text{Fe}_3\text{O}_4/\text{MgO}} = -0.55$ under the assumption that the polarization of MgO/Fe ($P_{\text{Fe}/\text{MgO}}$) is 0.7 based on the TMR ratio of $\text{Fe}/\text{MgO}/\text{Fe}$ at 9 K [29]. At room temperature, $P_{\text{Fe}_3\text{O}_4/\text{MgO}}$ is estimated to be 0.09, under the assumption that $P_{\text{Fe}/\text{MgO}} = 0.56$ at 300 K based on Ref. [30]. $P_{\text{Fe}_3\text{O}_4}$ may be underestimated because $P_{\text{Fe}/\text{MgO}}$ in $\text{Fe}_3\text{O}_4/\text{MgO}/\text{Fe}$ may be smaller than that in $\text{Fe}/\text{MgO}/\text{Fe}$ because annealing is not performed after deposition of the upper electrode. Although the TMR ratios differ between room temperature and 80 K, the magnetic fields of the maximum TMR, which are associated with magnetic characteristics, are very similar, as shown in Fig. 2(a).

Note that the TMR ratio of -55.8% is derived by the conventional definition of

$$\text{TMR}(\%) = \frac{(R_{\text{AP}} - R_{\text{P}})}{R_{\text{P}}} \times 100, \quad (1)$$

where R_{P} and R_{AP} are the tunnel resistance for parallel and antiparallel magnetic configurations, respectively. In conventional MTJs, such as $\text{Fe}/\text{MgO}/\text{Fe}$, definition (1) is called the “optimistic definition” because the maximum TMR ratio reaches infinity. However, in the case of inverse TMR observed in $\text{Fe}_3\text{O}_4/\text{MgO}/\text{Fe}$, the maximum value is limited to 100% by this definition. There is another definition as follows:

$$\text{TMR}(\%) = \frac{(R_{\text{AP}} - R_{\text{P}})}{R_{\text{AP}}} \times 100, \quad (2)$$

which is called the pessimistic definition for conventional MTJs because the maximum ratio is 100%, although it is an “optimistic” definition for inverse TMR. Note that the inverse TMR of -55.8% calculated by definition (1) corresponds to -126% by definition (2). The shape of the TMR curve is sharp at its maximum, which indicates a reduced antiparallel state, meaning that there is still some room for improvement in the TMR ratio.

The TMR curves for Sample 3 are shown in Fig. 2(b). At 80 K, the TMR ratio is only -22.5% , which is smaller than that for Sample 1. In addition, the shape of the TMR curve broadens to higher magnetic fields at low temperatures, implying that the magnetic characteristics vary. The change of the magnetic property of Sample 3 is also confirmed by comparison of magnetic hysteresis between high and low temperature, as shown in Fig. S3 of the Supplemental Material [28]. At low temperature, $\text{Fe}_3\text{O}_4/\text{MgO}/\text{Fe}$ multilayer shows a clear two-step hysteresis loop with large coercive field, although the hysteresis is narrow at high temperature because of close coercive field between Fe_3O_4 and Fe, like Sample 1.

The shapes of TMR curves are not square, which is different from that in a conventional MTJ like $\text{Co-Fe-B}/\text{MgO}/\text{Co-Fe-B}$. This could be attributed to the moderate magnetic reversal of Fe_3O_4 and aforementioned close coercive field between Fe_3O_4 and Fe. The anisotropic magnetoresistance (AMR) of Fe_3O_4 can be included in the background of the TMR curves. However, it should be a small effect because the AMR of Fe_3O_4 is much smaller than the TMR and the sign of the effect is opposite (see Fig. S4 in the Supplemental Material [28]).

To understand the difference between Samples 1 and 3, we investigate the temperature dependence of TMR ratio for the three samples, as shown in Fig. 3(a). At room temperature, all the TMR ratios are about -10% , and the absolute values then increase with decreasing temperature. For Sample 1, the TMR ratio increases monotonically as the temperature decreases to 80 K, whereas the TMR for Samples 2 and 3 exhibits a maximum at 125 K. At all temperatures, the TMR ratio of Sample 3 is larger than that of Sample 2. The TMR ratios strongly depend on the O_2 atmosphere during the formation of Fe_3O_4 , and

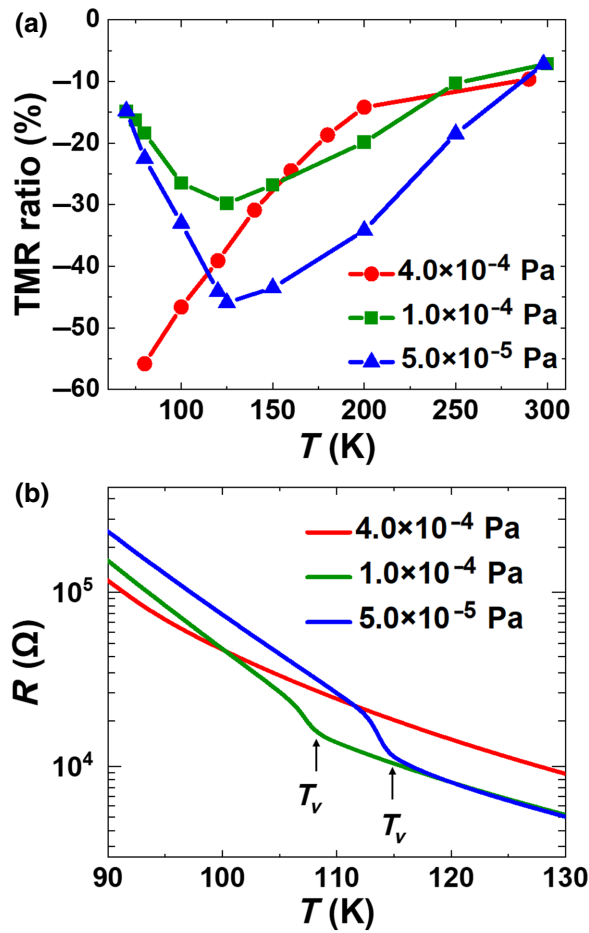


FIG. 3. (a) Temperature dependence of TMR ratio of the MTJs. The resistance at 2000 Oe is employed as R_p . (b) Resistance of Fe_3O_4 electrodes deposited in various oxygen atmospheres.

exhibit a maximum at the Verwey temperature, which is a well-known phase transition in Fe_3O_4 [30–32].

To confirm the Verwey temperature of each MTJ, we measure the temperature dependence of the resistance of Fe_3O_4 electrodes, as shown in Fig. 3(b). All the Fe_3O_4 electrodes exhibit an exponential increase in resistance, and Samples 2 and 3 exhibit an abrupt increase in resistance at 108 and 114 K, respectively. In contrast, Sample 1 exhibits no significant change in resistivity from 300 to 80 K, the same as the TMR ratio. This result strongly supports that the Verwey transition is responsible for the temperature dependence of TMR shown in Fig. 3(a). Note that Sample 3, for which the TMR ratio is larger than Sample 2, has a higher Verwey temperature that is closer to that of the bulk material.

For Sample 1, there remains a possibility that the Fe_3O_4 is overoxidized, resulting in the presence of the $\gamma\text{-Fe}_2\text{O}_3$ phase. Since both Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ form a spinel structure and the lattice constants are almost the same, it is difficult to distinguish them using XRD [33]. Thus, as

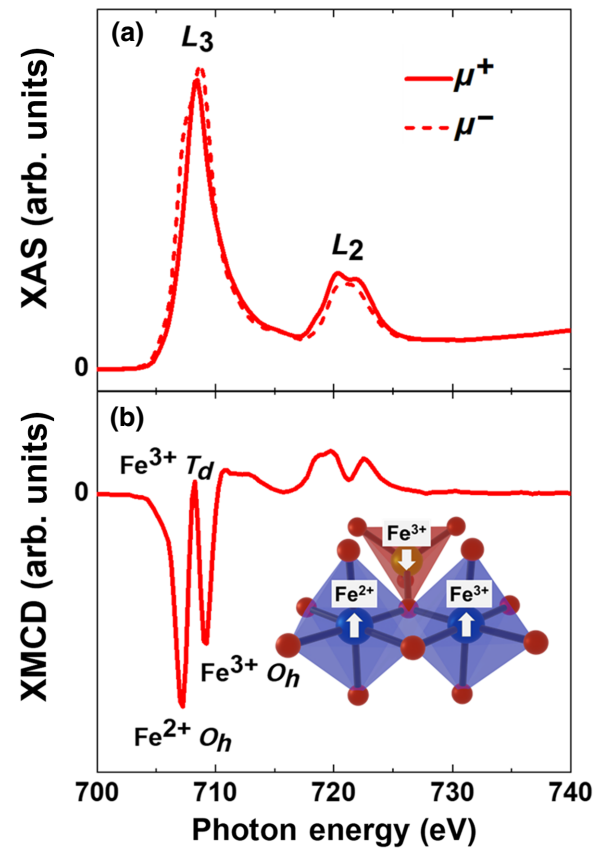


FIG. 4. (a) XAS and (b) XMCD of 50-nm-thick Fe_3O_4 films prepared under oxygen pressure of 4×10^{-4} Pa (Sample 1). Inset shows an illustration for A (red) and B (blue) sites.

shown in Fig. 4, we conduct XAS and XMCD of 50-nm-thick $\text{Fe}_3\text{O}_4(001)$ films prepared using an oxygen partial pressure of 4×10^{-4} Pa with a 1-nm-thick MgO capping layer. The complex differential spectral line shape in the L_3 and L_2 edge XMCD corresponds to the overlapping of three kinds of Fe site multiplet structures with antiparallel coupling. The XMCD line shape indicates the formation of a spinel-type structure because the spin-down states of Fe^{2+} and Fe^{3+} in O_h symmetry (B site) with spin-up states of Fe^{3+} (T_d : A site) can be clearly seen as antiparallel coupling. The intensity of the Fe^{2+} component can be monitored by the degree of oxidation. Within the probing depth of XAS and XMCD of 3 nm from the sample surface, the interfacial regions are detected, including the capping MgO layer. The intensities of Fe^{2+} and Fe^{3+} in O_h are almost similar to those of previous studies of XMCD in Fe_3O_4 [34–37], meaning that the Fe_3O_4 with stoichiometric B site is synthesized, but the Verwey transition is absent in Sample 1. Since the Verwey transition has been reported to be very sensitive to oxygen composition [38,39], the O_2 partial pressure significantly influences the transport of Fe_3O_4 . Compared with previous reports [37,40], the ratio

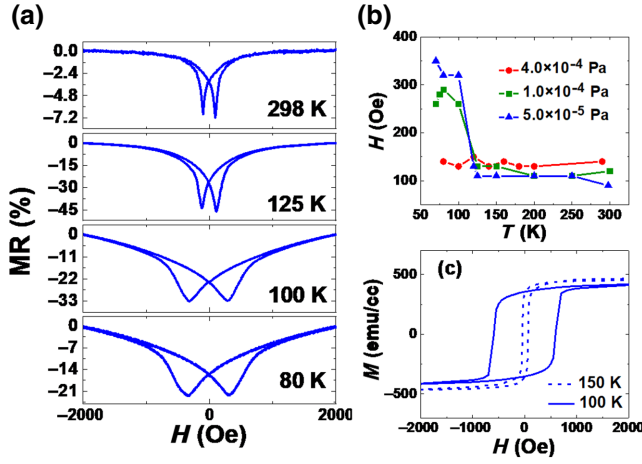


FIG. 5. (a) TMR curves for $\text{Fe}_3\text{O}_4(001)/\text{MgO}(001)/\text{Fe}(001)$ deposited at 5×10^{-5} Pa at various temperatures. (b) Temperature dependence of the magnetic field where the TMR ratio exhibits maximum values. (c) Magnetic hysteresis curves of an $\text{Fe}_3\text{O}_4(001)$ film deposited at 5×10^{-5} Pa above and below the Verwey temperature.

of $\text{Fe}^{3+}(T_d)$ component decreased, meaning less occupation of A sites. At the moment, it is not conclusively known whether A site vacancies contribute to the large TMR ratio because Fe^{3+} in A site provides no conduction electrons. Further investigations are required to clarify the role of the A site in Fe_3O_4 for TMR.

The shape of the TMR curves also provides clues for understanding TMR. In Fig. 5(a), the TMR curves of Sample 3 are shown in terms of temperature. From 298 to 125 K, the tunnel resistance exhibits peaks at ± 100 Oe, whereas at temperatures under 100 K, the coercive field for TMR suddenly increases to ± 320 Oe. The switching magnetic fields are plotted in Fig. 5(b) as functions of temperature. It is apparent that the Verwey transition enhances the coercive magnetic fields of Fe_3O_4 below the Verwey temperature [41,42]. The change in coercive force of Fe_3O_4 films is also confirmed by superconducting quantum interference device measurements of $\text{MgO}(100)/\text{Fe}_3\text{O}_4(50 \text{ nm})$ film, as shown in Fig. 5(c).

Since we use a MgO/Fe counter electrode, the tunneling process, namely coherent or diffusive tunneling, needs to be discussed. In $\text{Fe}/\text{MgO}/\text{Fe}$ MTJs, since coherent tunneling through the Δ_1 band dominates the transport, a large TMR is observed. The Δ_1 band consists of s , p_z , and $d_{3z^2-r^2}$. In addition, if we consider a simple picture of the transport in Fe_3O_4 , the main contributions to the transport are the t_{2g} states, which consist of d_{xy} , d_{yz} , and d_{zx} orbital symmetries. Since the wave functions of the t_{2g} state of Fe_3O_4 and the Δ_1 band of Fe are not hybridized, the tunneling process via the t_{2g} state may be diffusive tunneling in the $\text{Fe}_3\text{O}_4/\text{MgO}/\text{Fe}(001)$ junction. To see the coherent tunneling in $\text{Fe}_3\text{O}_4/\text{MgO}/\text{Fe}$ in detail, we calculate

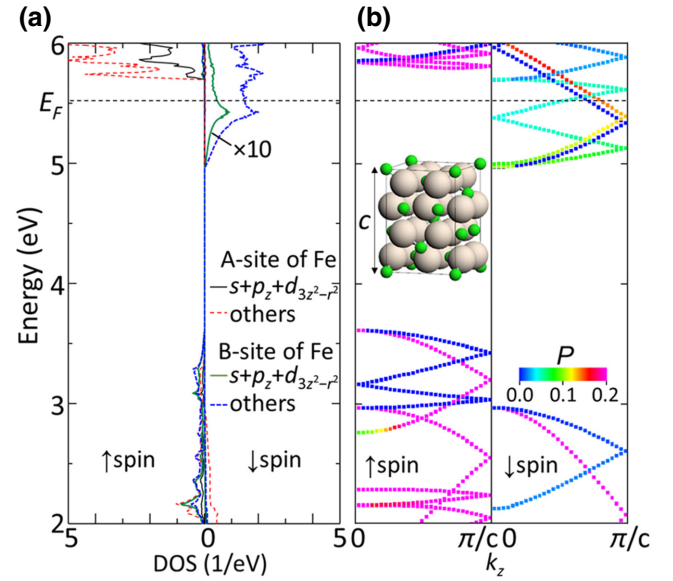


FIG. 6. Calculation results of (a) spin-dependent local density of states (DOS) and (b) $E-k$ dispersion relation between $\mathbf{k} = (0, 0, 0)$ and $\mathbf{k} = (0, 0, \pi/c)$. The unit cell for $E-k$ calculations is shown in (b). In (a), the DOS of the sum of the s , p_z , and $d_{3z^2-r^2}$ orbitals (the coherent orbitals) of the B site of Fe ions in the conduction band is shown magnified 10 times. The percentages of the summation of the coherent orbitals (P), which are hybridized with the wave functions transmitted through MgO in an $\text{Fe}_3\text{O}_4/\text{MgO}/\text{Fe}$ junction, are plotted in color.

the electronic structure for an optimized Fe_3O_4 supercell structure, as shown in Fig. 6(b). We call the s , p_z , and $d_{3z^2-r^2}$ orbitals of Fe_3O_4 the coherent orbitals, and other orbitals the diffusive orbitals. The first-principles calculation is performed using the VASP code with the PAW potentials [43] in the generalized gradient approximation with Perdew-Burke-Ernzerhof functional [44,45]. A correction of the Coulomb interaction U of 4.5 eV is assumed for the Fe ions [46,47]. The cutoff energy is set to 400 eV and the crystal momentum k sampling mesh is set to $(k_x, k_y, k_z) = 21, 21, 21$.

Figure 6(a) shows the density of states for spin-up and spin-down states. Since the spin-down states cross the Fermi level (E_F), half-metallicity is reproduced. At E_F , the diffusive orbitals of the B site of the Fe ion with spin down (thick blue dotted curve) mainly cross the small contribution of the coherent orbitals (thick green solid curve). Figure 6(b) shows the energy-momentum ($E-k$) dispersion relation along $(k_x, k_y, k_z) = (0, 0, 0) \rightarrow (0, 0, \pi/c)$ in the Brillouin zone. The color of the plot indicates the percentage of the sum of the coherent orbitals, which hybridize with the Δ_1 band at the interface with the Fe electrode layer. The bands near E_F contain about 10% of the coherent orbitals. Therefore, the coherent tunneling can take place with these bands in Fe_3O_4 . Another possibility is diffusive transport via scattering at the $\text{Fe}_3\text{O}_4/\text{MgO}$ interface

due to the symmetry mismatch of the wave functions. The half-metallicity of Fe_3O_4 can bring about large TMR even though the tunneling is not coherent.

Important clues for distinguishing between coherent and diffusive tunneling can be found by comparing a MTJ with a MgO barrier and an amorphous Al_2O_3 barrier. Further development of the fabrication techniques for MTJs using Fe_3O_4 is necessary in order to investigate the tunneling process experimentally.

IV. CONCLUSION

In conclusion, we fabricate MTJs of $\text{Fe}_3\text{O}_4(001)/\text{MgO}(001)/\text{Fe}(001)$, the quality of which is confirmed by XRD and XMCD. The MTJs exhibit a large inverse TMR effect of -55.8% , which is comparable with the theoretical prediction. If we use an optimistic definition for the inverse TMR, the TMR ratio achieves 126% , which is the largest value for Fe_3O_4 MTJs. We find that the TMR ratio strongly depends on the deposition conditions of the Fe_3O_4 layer, which may be attributable to the Verwey transition in Fe_3O_4 . The possibility of coherent tunneling is discussed on the basis of *ab initio* calculations through the s , p_z , and $d_{3z^2-r^2}$ orbitals in Fe_3O_4 at the Fermi level, which are hybridized with the Δ_1 band of Fe via the MgO tunnel barrier. These results obtained in this study could pave the way for the development of high-functional fully oxide spintronic devices.

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