

Surface and Interface Magnetism from Mössbauer Spectroscopy Using Surface-Selectively Enriched Samples

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By UHV deposition technique, very thin ^{57}Fe layer was deposited on a thick ^{56}Fe film and the magnetic properties of Fe interfaces in contact with various non-magnetic materials were studied from Mössbauer spectroscopy. The initial stage of Fe surface oxidation was studied with air-exposed samples. Surface-selectively enrichment was also attempted by a wet method and the surface magnetic properties of $\alpha\text{-Fe}_2\text{O}_3$ were investigated.

KEY WORDS: Interface magnetism/ Mössbauer spectroscopy/ Thin films/ Surface oxidation/

INTRODUCTION

Mössbauer spectroscopy has been applied to study surface and interface phenomena in several ways.¹⁾ Conversion electron Mössbauer measurements (CEMS) in a backscattering geometry are most commonly used to study corrosion and catalysis problems. By analyzing the energy of conversion electron, the depth range of the observation can be confined to some extent. However, even with this depth-selective conversion electron Mössbauer spectroscopy (DCEMS), the depth range of the observation is not much smaller than 10 nm. The resolution is not enough to catch electronic and magnetic surface effects.

Some years ago, the authors have studied the surfaces of ferromagnetic Fe and Co metals using electrolytically deposited ^{57}Co source atoms as the microprobes. The obtained results have evidenced the absence of magnetically dead layers proposed by Liebermann *et al.*, from their magnetic measurements on electrolytically deposited thin films. In using radioactive isotopes as the probes for the surface studies, some experimental inconveniences are unavoidable and hence this technique can not be extensively applied.

In contrast, the surface-selectively enriched samples are very useful for many purposes. Recent developments in the authors' group are introduced in this article. The magnetic properties of Fe metal interfaces in contact with various non-magnetic materials were studied using surface-selectively enriched samples prepared by ultra-high vacuum (UHV) deposition. In the next chapter, the results are briefly summarized. The third chapter shows the results on very thin oxide layer formed on the surface of Fe metal using air-exposed samples. Surface-selectively enrichment

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was also attempted by a wet method in an aqueous solution and the surface magnetic behaviors of $\alpha\text{-Fe}_2\text{O}_3$ particles were investigated. The results are described in the last chapter.

Fe METAL INTERFACES

Figure 1 shows typical structures of the prepared samples for the study of Fe interfaces of thick Fe metal films. In UHV atmosphere (10^{-7} Pa during the deposition), a very thin ^{57}Fe layer is deposited on a pure ^{56}Fe substrate (~ 10 nm) and

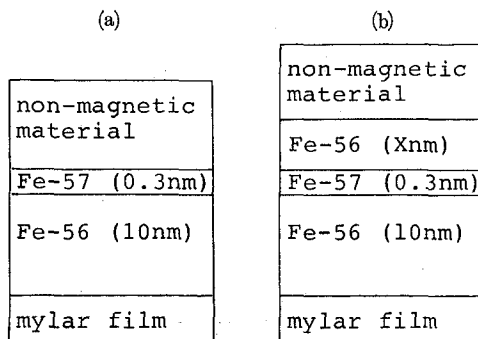


Fig. 1. Schematic illustration of the structures of prepared samples for the study of Fe interfaces in contact with non-magnetic materials.

the surface is covered by a non-magnetic material. Normally an Fe film thicker than 5 nm is a continuous layer and exhibits the bulk Mössbauer spectrum. Using such a film as shown in Fig. 1 (a), we observe the interface properties of a rather thick Fe film, since the Mössbauer probe, ^{57}Fe , is only located at the topmost region of the interface. Thus we study the interface effect excluding any thickness effect. For a depth-profiling measurement, another ^{56}Fe layer with a certain thickness is deposited on the ^{57}Fe layer (Fig. 1 (b)).

As an example, the result on Fe interfaces in contact with V metal is shown here. Figure 2 shows the Mössbauer spectra for three depth ranges. The spectrum for the depth range of 0.7–1.05 nm is a normal six-line pattern. From a viewpoint of magnetism, the interface effect does not extend to this depth. The spectrum for 0.35–0.7 nm is also a six-line pattern but with slightly broadened widths, suggesting the existence of reduced hyperfine field components. A remarkably different spectrum was obtained for the topmost interface region, 0–0.35 nm. The broad line widths suggest a considerable distribution of the hyperfine field. Assuming a constant isomer shift and no quadrupole interaction for simplicity, the distribution of the hyperfine field was analyzed and the obtained best fit is shown in the inserted figure. Although the distribution of the hyperfine field is wide and rather continuous, two peaks are identified in the curve, approximately at 24 T and 32 T, respectively. The average thickness of 0.35 nm roughly corresponds to two atom layers, as far as the ^{57}Fe layer is uniform. It is then reasonable to attribute the two hyperfine fields to two interface atom layers. 24 T represents the hyperfine field at the

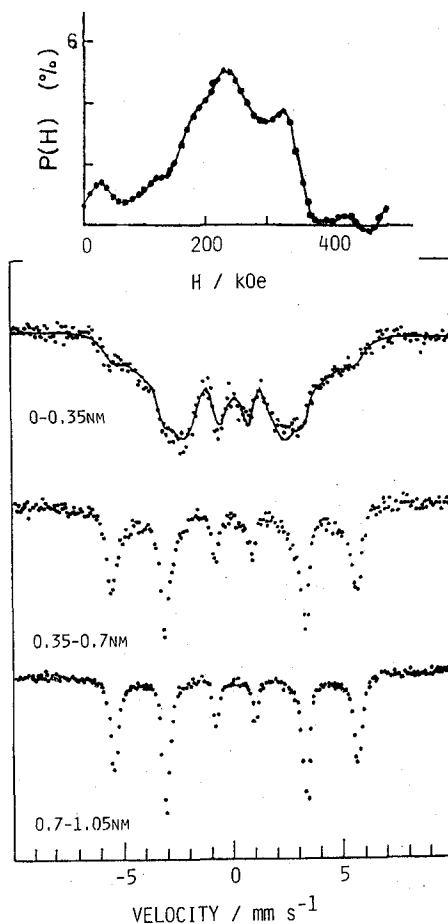


Fig. 2. Mössbauer absorption spectra at 4.2 K of Fe interfaces in contact with V metal for three depth regions. Inserted is the assumed distribution of the hyperfine field to account for the spectrum of the topmost interface region.

top interface atom layer and 32 T the value at the second layer. Assuming the rough proportionality of the hyperfine field with the local magnetic moment, we get the following conclusion; the reduction at the top interface layer would be about 30% in the average. However the second atom layer has a comparable magnetic moment to the standard value. The perturbation of the magnetization due to the interface effect is negligible at further atom layers.

Measurements were carried out on Fe interfaces overcoated with various non-magnetic materials and the results are summarized in a schematic illustration (Fig. 3).²⁻⁴⁾ Similar to the case of V-coating, a decrease of magnetization at the interface atom was observed in Cu-, Sb- and Mg-coating interfaces. On the other hand, an enhancement of interface magnetization was suggested in the cases of MgF₂- and MgO-coating. A slight increase of the hyperfine field was also observed by Owens *et al.* at the Ag-coated Fe interface.⁵⁾ The interface effect due to Pd-coating is

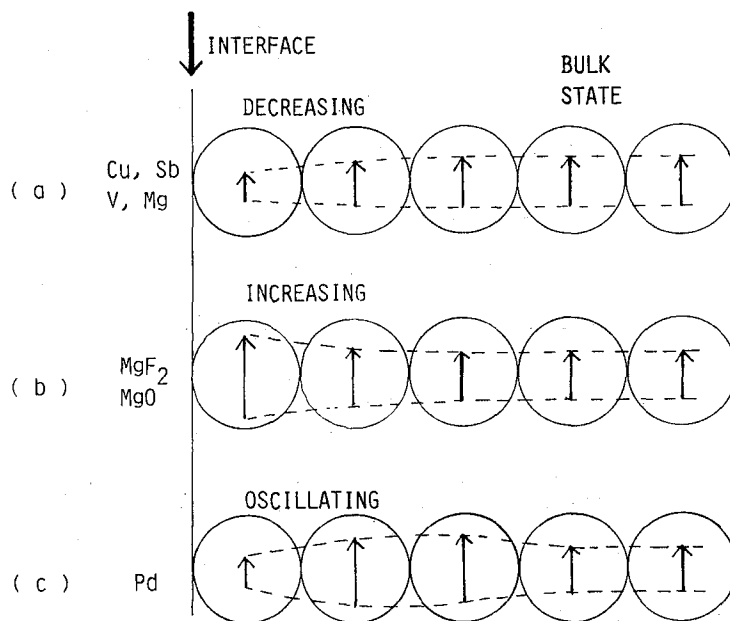


Fig. 3. Variation of local magnetic moments of Fe atoms at the interfaces contacting various non-magnetic materials.

complicated as shown in Fig. 3 (c). In all cases, the magnetic interface effect is confined within a few atomic layers from the interface boundary.

Fe-V interfaces were theoretically studied by Hamada *et al.*⁶⁾ They have calculated the band structure of a thin film consisting of three Fe and three V atom layers assuming the stacking with (110) plane. The result suggests that the magnetic moments for Fe atoms at the interface and inner sites are 1.90 and $2.20 \mu_B$, respectively. Qualitatively the decrease of the magnetic moment at the interface site is consistent with the present result. On the other hand, Ohnishi *et al.* have calculated the electronic structure of an Fe film with seven atom layer thickness and suggested a considerable enhancement of the surface magnetic moment in a vacuum surface; $2.98 \mu_B$ at the top surface layer of (100) Fe plane.⁷⁾ It is of interest to compare this result with the Mössbauer observation on MgF_2 - or MgO -coating surface. It seems that the increase of the hyperfine field may occur if the 3d electronic structure of the surface Fe atom is not significantly modified by the chemical bonding with the coating material. The behavior of Pd-coating interface may be interpreted as a result of two competing mechanisms, increase of magnetic moment in a slightly longer range and decrease, which is drastic only at the topmost layer.

By alternate deposition of two elements, we have prepared multilayered films with artificial superstructures and interface magnetism study with combining neutron diffraction and NMR is in progress.^{8,9)}

SURFACE OXIDATION

Surface-selectively enriched samples are also useful for the study of very thin

oxide layers on Fe surfaces.¹⁰⁾ By UHV deposition, pure ^{56}Fe layer with the thickness of 21 nm was prepared and on the surface, ^{57}Fe with 2 nm was deposited. After the sample had been exposed to air, Mössbauer measurements were performed at 4.2K and 300K. Figure 4 shows the spectrum at 4.2K, which can be decomposed into two part; metallic and oxidized fractions.

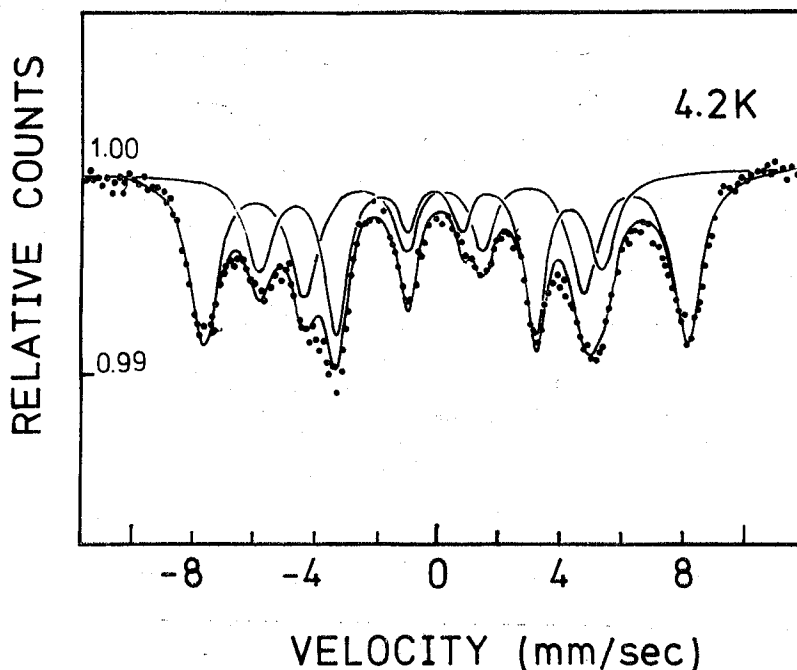


Fig. 4. Mössbauer spectrum at 4.2 K for a surface-selectively enriched sample after air-exposed.

The average hyperfine field for the metallic part is 35 T, which is slightly larger than the standard bulk value, 34 T. The increase may be accounted for as an interface effect. As was introduced in the preceding chapter, the hyperfine field at the interface with MgO is larger than the bulk value. At the interface in contact with Fe oxide layer, the hyperfine field seems to be increased. The intensity ratio of the metallic six-line pattern is close to 3:4:1:1:4:3, which indicates that the magnetization is oriented in the film plane. Since the total thickness of the Fe layer is only about 23 nm, the magnetization should be oriented in plane by the shape anisotropy.

The average hyperfine field of the oxide part was found to be 49 T. Only an Fe^{3+} absorption was observed and no Fe^{2+} absorption was appreciable. The relative intensity ratio of the six lines is nearly 3:2:1:1:2:3. Probably this result is due to the non-collinear spin arrangement, which often occurs in ultrafine particles or extremely thin films.¹¹⁾ The ratio of the absorptions for the metallic and oxide parts was estimated to be 41:59. If the recoilless fractions for both phases are the same, the relative volume of the oxide phase is 59% of the total ^{57}Fe . If the depo-

sition of ^{57}Fe was uniform and if the oxide has a layered structure, the average thickness of the oxide should be 1.2 nm in the metal Fe form. If the density of $\gamma\text{-Fe}_2\text{O}_3$ is assumed, the oxide thickness is estimated to be 2.1 nm.

The spectrum at 300K for the same sample (Sample-I) is shown in Fig. 5, with

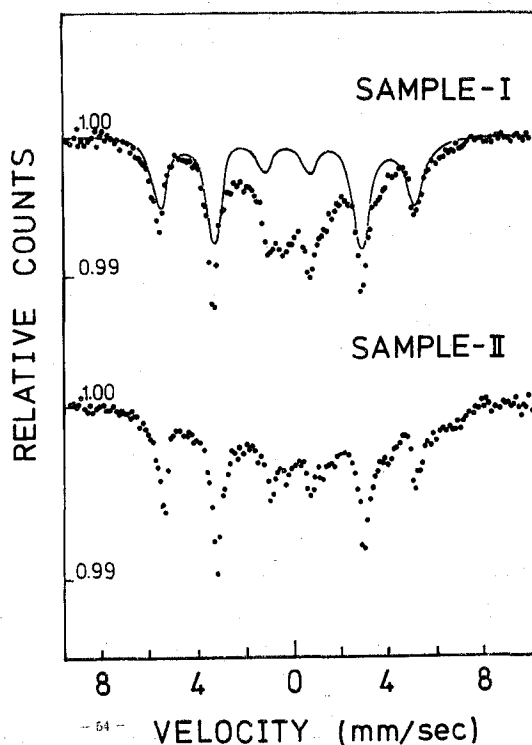


Fig. 5. Mössbauer spectra at 300 K of air-exposed surface-selectively enriched samples.

the result for a similar sample (Sample-II). The six lines for the metallic part are clear but the oxide absorption has a very broad line profile. To fit this broad spectrum, not only the distribution of hyperfine field but also the distribution of the superparamagnetic relaxation time should be taken into account and accordingly no unique solution is obtained. Therefore the oxide absorption area was estimated with reducing the metallic absorption from the total absorption area. Thus the relative oxide absorption was estimated to be 57% of the total ^{57}Fe . This value is very close to the value, 59%, at 4.2K.

The reproducibility of the broad spectrum at 300K was confirmed by Sample-II, with the same structure as Sample-I. If the relative volume of such oxide layers in the absorber is small, it is difficult to estimate the line profile or the absorption area. It is to be noted that not only at room temperature but also at lower temperatures, Mössbauer measurements should be carried out.

The distribution of the hyperfine field at 300K in the oxide layer extends up to about 40 T. Therefore it is certain that this oxide layer does not correspond to

α -, β - or γ -FeOOH. The bulk hyperfine field at 300K for α -FeOOH is 37 T and the Néel temperatures for β - and γ -FeOOH are below 300K. The spectrum at 4.2K does not agree with that of α -Fe₂O₃. This oxide probably is similar to γ -Fe₂O₃ whose average hyperfine field at 4.2K in the bulk form is 50.5 T.

Using surface-selectively enriched samples, very thin oxide layer on Fe surfaces are investigated. If the surface is coated by other material, we can study the oxidation process under a coating layer. Measurements on Fe interface overcoated by Sb with different thicknesses are in progress.¹²⁾

SURFACE OF Fe OXIDE

Surface magnetic properties of α -Fe₂O₃ have been studied using surface-selectively enriched samples.¹³⁾ In this case, the samples were prepared not by vacuum deposition but by a wet method in aqueous solutions. α -Fe₂O₃ particles were obtained by thermal decomposition of FeSO₄·H₂O prepared from pure ⁵⁶Fe. The surface of α -⁵⁶Fe₂O₃ particles was coated with very thin ⁵⁷Fe layers by the following procedure. A suspension with pH=2.6, containing dilute ⁵⁷Fe (III) chloride and α -⁵⁶Fe₂O₃ particles was subjected to aging at 90°C for 20 h. The amount of ⁵⁷Fe corresponds to monatomic layer on the surface.

Figure 6 shows the Mössbauer spectra at 300K and 4.2K of the surface-selectively enriched α -Fe₂O₃. At 4.2K the hyperfine field is nearly the same as the bulk value. On the other hand, at 300K, the hyperfine field is significantly smaller

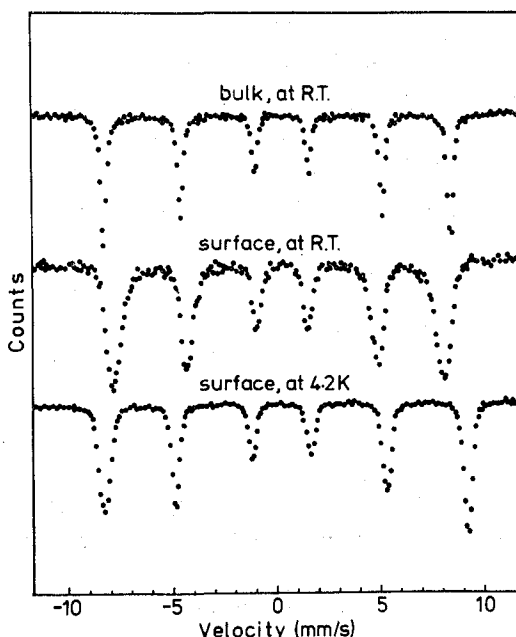


Fig. 6. Mössbauer spectra at 300 K and 4.2 K for surface-selectively enriched α -Fe₂O₃. For reference the spectrum at 300 K for standard α -Fe₂O₃ also is shown.

than the normal α -Fe₂O₃ as also shown in the same figure. The temperature dependence of the surface hyperfine field is shown in Fig. 7. For comparison, the behavior of bulk α -Fe₂O₃ and the Brillouin curve for $S=5/2$ are also shown. It is obvious that the temperature dependence of the surface hyperfine field is much greater than the bulk curve. It is interesting to compare this result with that of γ -Fe₂O₃ surface, which was previously reported by the present authors.¹⁴⁾ ⁵⁷Co Mössbauer source atoms were deposited on the surface of γ -Fe₂O₃ and Mössbauer source spectra were measured. In these two oxides, the temperature dependences of the surface hyperfine field are very similar, as shown in the figure.

The temperature dependence is qualitatively accounted for by using a simple molecular field approximation. At a surface site, the exchange field is smaller than the bulk value because the number of neighboring magnetic ions is less. If the exchange field is assumed to be 60% of the normal value, the temperature dependence is satisfactorily reproduced. The calculated curve is shown by the broken line in Fig. 7. Such a temperature dependence is one of the characteristics of sur-

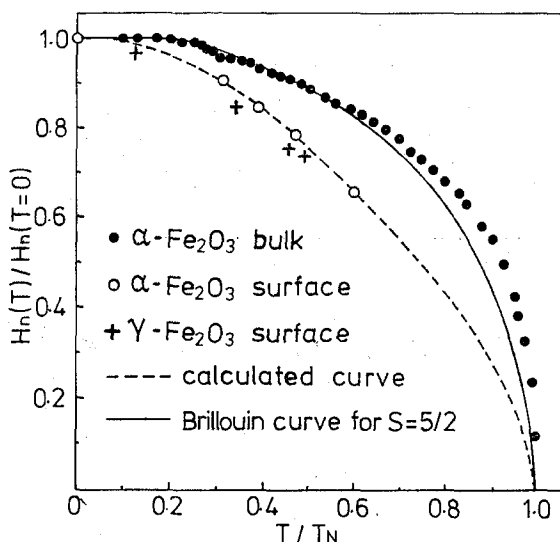


Fig. 7. Temperature dependence of the surface hyperfine field of α -Fe₂O₃. The results on γ -Fe₂O₃ also are shown.

face magnetic behaviors and a similar result was obtained in a photoemitted electron spin measurement on Fe₃O₄ surface.¹⁵⁾

It is no doubt that surface-selectively enriched samples are very useful for the study of surface and interface phenomena and will be used more extensively.

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REFERENCES

- (1) T. Shinjo, *J. Phys. (Paris)*, **40**, C2-63 (1979).
- (2) J. Lauer, W. Keune and T. Shinjo, *Physica*, **86-88B**, 1407 (1977).
- (3) S. Hine, T. Shinjo and T. Takada, *J. Phys. Soc. Jpn.*, **47**, 767 (1979).
- (4) N. Hosoiito, T. Shinjo and T. Takada, *J. Phys. Soc. Jpn.*, **50**, 1903 (1981).
- (5) A.H. Owens, C.L. Chien and J.C. Walker, *J. Phys. (France)* **40**, C2-74 (1979).
- (6) N. Hamada, K. Terakura and A. Yanase, *J. Magn. & Magn. Mater.* **35**, 7 (1983) and private communication.
- (7) S. Ohnishi, A.J. Freeman and M. Weinert, *J. Magn. & Magn. Mater.* **31-34**, 889 (1983).
- (8) T. Shinjo, N. Hosoiito, K. Kawaguchi, T. Takada, Y. Endoh, Y. Ajiro and J M. Friedt, *J. Phys. Soc. Jpn.*, **52**, 3155 (1983).
- (9) A full report on Fe-V multilayers is in preparation.
- (10) A part of this work is preliminarily reported; T. Shinjo, T. Shigematsu, T. Iwasaki and T. Takada, *Jpn. J. Appl. Phys.*, **19**, L53 (1980).
- (11) e.g. A.H. Morrish and K. Haneda, *J. Magn. & Magn. Mater.* **35**, 105 (1983).
- (12) T. Shinjo, T. Iwasaki, T. Shigematsu and T. Takada, in preparation.
- (13) T. Shinjo, M. Kiyama, N. Sugita, K. Watanabe and T. Takada, *J. Magn. & Magn. Mater.* **35**, 133 (1983).
- (14) A. Ochi, K. Watanabe, M. Kiyama, T. Shinjo, Y. Bando and T. Takada, *J. Phys. Soc. Jpn.* 2777 (1981).
- (15) S.F. Alvarado, *Z. Phys.* **B33**, 51 (1979).