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SURFACE AND INTERFACE MAGNETISM BY MöSSBAUER SPECTROSCOPY

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1. Problems in surface magnetism.- In recent years magnetic properties of transition metal surfaces have been of great interest from a viewpoint of fundamental physics and also in connection with surface chemistry such as catalysis research. Magnetic behaviors near a surface or an interface in a magnetically ordered crystal may differ in many respects from those of the inside. For an understanding of the perturbation of magnetic order at a surface boundary, not only clean vacuum surfaces but also various kinds of interfaces are of importance.

The main problems to be considered here are local magnetic moment, the temperature dependence of surface magnetization and surface anisotropy. Before describing the information obtained from Mössbauer spectroscopy, experimental results by complementary methods will be briefly surveyed.

1.1. Local magnetic moment.- In the metallic case, a local magnetic moment sensitively depends on the local environment. First of all, the local magnetic moment of a surface atom at T = 0K must be made clear. Most studies on the surface magnetism have been done by using thin film samples and numerous papers have been published. The study of thin film magnetism has a rather long history but until recently the sensitivity of the measurements and the quality of the samples were not good enough to derive any significant information on surface magnetism.

Liebermann et al. have measured the magnetization of electrodeposited thin films of Fe, Co and Ni as a function of thickness and proposed the "dead layer model" to explain their results: namely the first surface layer has no magnetic moment. This conclusion is not generally believed but the term, dead layers, has been popularly used.

An investigation on epitaxial ferromagnetic thin films was reported by Gradmann /1,2/. By vacuum deposition, very thin epitaxial films of Fe-Ni alloy and Co, on Cu substrates, were prepared and the magnetization was measured by a sensitive torsion magnetometer. When the film was coated by Cu or Ag, the magnetization of the thin film was actually the same as the bulk value but when coated by Mn or C, a reduction of the magnetization was observed. The results suggest that the interface magnetic effect depends on the coating substance.

Koopke and Bergmann measured an anomalous Hall effect of very thin Fe films /3/. Their samples were vacuum deposited Fe films on cold substrates of amorphous alloys (Pb-Bi or Sn-Cu). The magnetisation of the films estimated for the Hall resistance was the same as the bulk value and it was concluded that the surface effect on the local magnetic moment is negligible.

A new technique to approach the interface magnetism was recently developed by neutron spectroscopists /4/. Sato and Abe measured the Bragg reflections of a multilayer sandwich film consisting of 20 Å Fe and 40 Å SiO layers, and estimated the magnetic anomaly at the interface, if any, to be less than 1/10 of one atomic layer's magnetization.

It seems that a remarkable surface effect on the local magnetic moment only occurs at the topmost layer, or extends at most to a few surface...
layers. In order to catch a surface anomaly by thin film measurements, the thickness of the sample has to be extremely thin. Not only the sensitivity of the measurements but also high accuracy in thickness determination is usually necessary. In addition to surface effects, various kinds of size effects may be included in the results. It is desirable to study a surface of bulk specimen. From this point of view, Mössbauer spectroscopy using $^{57}$Co or $^{57}$Fe as a microprobe on a surface is a useful method, as will be described below.

Newly developed experimental techniques which can observe magnetic properties of clean vacuum surfaces of bulk crystals are the polarization measurements of photoemitted, field emitted and tunneling electrons /6/. The electron spin polarization at a Ni surface was determined through electron capture by small angle reflected deuterons/7/. These measurements only detect the electrons near the surfaces. It is however very difficult to separate a surface information from the bulk properties since the mechanism of electron emission is complicated.

Theoretical works on local magnetic moments at a surface site have been published only recently. In most cases, calculations were based on a tight-binding model assuming a free surface of crystallographically simple plane. It is questionable to compare them quantitatively with experimental results on actual interfaces. However it is of interest to note the variety of the theoretical predictions.

Liebsch et al. showed the possibility of dead layers /8/. Fulde et al. suggested the existence of an antiferromagnetic surface layer /9/. According to Desjonqueres and Cyrot-Lackmann, the surface magnetic moments of Fe and Ni are nearly the same as the bulk values /10/. On the other hand, Teraoka and Kanamori suggested the enhancement of surface magnetic moment /11/.

An interesting theoretical prediction is the existence of "live layers" in the surface of Cr or V /11-13/. The possibility of local magnetic moment induced only at the surface has been discussed recently. At the moment, however, no Mössbauer experiment is relevant to this problem.

1.2. Temperature dependence of surface magnetization.- Because the number of magnetic neighbours is reduced at a surface site, the Weiss field is generally expected to be smaller than the inside. Therefore even when the surface magnetic moment is not changed, the temperature dependence of the local magnetization at the surface may be different from the bulk curve. Many calculations have been carried out for the cases of thin films and also surface layers, on condition that all the local magnetic moment at $T = 0K$ is the same even at the surface boundary. An example quoted here as figure 1 is a part of the computer works by Binder and Hohenberg /14/. It was suggested that the reduction of surface magnetization of this kind is only appreciable at relatively high temperatures. When the temperature approaches $T_C$, the surface effect extends more deeply into the crystal.

![Figure 1: Monte Carlo calculation for the magnetization in a Heisenberg system by Binder and Hohenberg /15/. The surface is (100) of a simple cubic lattice. The effective field boundary condition at $n = 16$ layers forces the magnetization to the bulk value.](image)

Concerning the temperature dependence of magnetization in a finite dimension, experimental studies are not fully following up the theoretical predictions. The temperature dependence of the magnetization of a very thin film, over the whole temperature range, is not possible to measure because of superparamagnetism and also because of chemical instability.

The temperature dependence of the surface
magnetization of a bulk crystal can be measured from
the observation of superlattice line of low energy
electron diffraction. The measurement near \( T_C \) on
NiO crystal has been reported by Palmberg et al. /15/ and lately by Namikawa /16/. Unfortunately
this method is only applicable to an antiferroma-
gnet.

1.3. Surface anisotropy.— In addition to the under-
standing of the local magnetic moment at a surface
atom, the direction of the surface spin is of in-
terest. A magnetic spin at a surface site has a
lower symmetry than in the bulk and anisotropic in-
teractions, which may be canceled by symmetry in
the interior need not to vanish at the surface. One
may assume that a surface atom has a symmetry axis
normal to the surface and therefore a strong aniso-
tropy can exist perpendicularly to the surface pla-
ne. Such a surface anisotropy only exists at the
topmost layers. As it is well known, the magnetiza-
tion of a ferromagnetic film is oriented parallel
to the plane due to the shape anisotropy. The ener-
gy of shape anisotropy and also the energy of crys-
talline anisotropy, per unit area of the film, de-
crease with a decrease of thickness. On the other
hand, the surface anisotropy per unit area remains
constant. In extremely thin films, by the surface
anisotropy, the magnetization may be oriented normal
to the film plane.

Gradmann firstly found the perpendicular
magnetization of very thin epitaxial films of Fe-Ni
alloy and Co when the thickness was as small as a
few Å /3/. Although the concept of surface anisotro-
py has sometimes been implicitly taken in the dis-
cussion of thin film magnetism, the existence of
surface anisotropy is clearly evidenced only by the
perpendicular magnetization, which was observed by
Gradmann's measurements and Mössbauer spectroscopy
as will be shown below.

Very recently the surface anisotropy in the case of
Ni was theoretically treated by Takayama et al.
/17/. A quantitative discussion of surface anisotro-
pv is very difficult especially in the metallic case
since a detailed knowledge on the electronic struc-
ture of the surface atom is necessary.

2. Mössbauer spectroscopic studies.—

2.1. Source spectroscopy.— The minimum activity of
\(^{57}\)Co required for Mössbauer sources is in the order
of 10 \( \mu\)Ci, whose amount is much less than one mono-
tomic layer in an area of 1cm\(^2\). If \(^{57}\)Co atoms are
uniformly deposited on a crystal surface, the Möss-
bauer emission spectra will give us information on
the top surface layer of a bulk crystal. The com-
mercial carrier-free \(^{57}\)Co solution has a suffi-
ciently high purity for this purpose. In metalic cases,
the emission spectroscopy always observes the stable
electronic state of \(^{57}\)Fe atom and the emission spec-
tra is essentially the same as the absorption spec-
tra. The problem actually is : how to deposit the
tracer amount of \(^{57}\)Co on a well-defined surface.

The author's group already published some
results on the surfaces of Fe and Co where the \(^{57}\)Co
source atoms were deposited by electrolytic means.
on an Fe plate, natural Fe layers were electrolyti-
cally deposited in advance and successively \(^{57}\)Co was
deposited on the surface /18/. After finishing the
deposition, the sample was cooled rapidly by liquid
nitrogen. The Mössbauer spectra at 4.2 K showed that
the state of \(^{57}\)Fe atoms was metallic and ferromag-
etic. The absence of any paramagnetic or oxidized
fraction was certified also from the spectra. The
hyperfine field was fairly distributed and the aver-
age (290 kOe) was smaller than the bulk value (340
kOe). The intensity ratio of the six lines was
nearly 3:4:1:1:4:3, which indicates that the magne-
tic spins are oriented parallel to the surface pla-
ne. No significant temperature dependence was obser-
ved between liquid nitrogen and liquid helium tem-
peratures. The sample was not stable above liquid
nitrogen temperature.

Similar results were obtained for \(^{57}\)Co on a
surface of bulk Co (hcp structure) and also on a
surface of a Co film deposited on a Cu substrate
(fcc structure) /19/. The surfaces in these measu-
rements were inevitably covered by ice, however,
the state of Fe was always ferromagnetic and no
dead layer was observed. It should be noted that the
films of Liebermann et al. who claimed the existen-
c of dead layers, also were electrolytically prepa-
red.

Vacuum depositions of \(^{57}\)Co were attempted by
Burton and Godwin to study the behavior of Fe impur-
rities on the surfaces of W and Ag /20/ and lately
by Mourey et al. to examine the single crystal sur-
face of Zn /21/. However the main interest in these
investigations was the lattice dynamical charac-
teristics of surfaces and no report has been published
yet concerning a ferromagnetic metal surface with
vacuum deposited \(^{57}\)Co as a source. Although there
are some experimental difficulties, \(^{57}\)Co source
spectroscopy using UHV deposition is a unique tech-
nique to study surface magnetic properties of bulk
single crystals.
2.2. Absorbers with enriched surfaces. - In order to enhance the surface features in the Mössbauer absorption spectra, it is useful to enrich selectively the surfaces with $^{57}$Fe. Van der Kraan firstly tried to coat fine particles of α-Fe$_2$O$_3$ with thin $^{57}$Fe$_2$O$_3$ layers [22] and recently Morrish et al. attempted to prepare $^{57}$Fe$_2$O$_3$-coated γ-Fe$_2$O$_3$ [23]. Lauer et al. adopted this idea for UHV deposited thin films. They prepared, for instance, a film consisting of Cu, 100 Å natural Fe, 5 Å $^{57}$Fe and Cu layers [24]. The hyperfine field at 4.2 K of the surface fraction was determined to be about 290 kOe, which is 15% smaller than the bulk.

If the isotope $^{56}$Fe is used as the base, instead of natural Fe, the surface enrichment in $^{57}$Fe becomes more effective. The author's group prepared some UHV deposited films composed of $^{56}$Fe and $^{57}$Fe layers. The structures of the multilayer films are schematically shown in figure 2a. The surface was coated by Sb in one case and by MgF$_2$ in the other case. An Fe film with the thickness of 100 Å exhibits nearly bulk magnetic properties [25, 26]. The temperature of the substrate during the deposition was low enough to prevent diffusion, thus most of $^{57}$Fe nuclei would be located in the surface layers and the Mössbauer spectra are expected to show the surface behavior of a rather thick film.

![Fig. 2a: Structure of the multilayer films. Sb and MgF$_2$ layers are thicker than 200 Å.](image)

By the external field, the line shapes of the first and the sixth lines were not greatly changed. The line broadening is mainly due to the distribution of the hyperfine field. The determination of the hyperfine field distribution by computer fitting is not yet completed but visually it appears that the surface effects in the two cases act in the opposite directions: reduction of the hyperfine field in the Sb-coated case and increase of the hyperfine field in the MgF$_2$-coated case.

Such an increase of the hyperfine field at the surface was also detected in the cases of Ag-coated surface [27], MgO-coated surface [28] and granular Fe-SiO$_2$ films [29]. On the other hand the decrease of the surface hyperfine field was found in the electrodeposited surfaces [18, 19] and Cu-coated surface [24]. It seems that the surface magnetic moment is not always smaller but is sometimes bigger than the bulk's moment. The surface magnetic effect is complicated and probably not explained by a simple mechanism.

2.3. Thin films. - Some problems in surface magne-
An example is the surface anisotropy whose effect is negligible in thick films. It is well known that the average orientation of the magnetic spins is determined by the relative intensity ratio of the spectrum. Interesting results were obtained with MgO-coated thin Fe films. For thick films, an intensity ratio of 3:4:1:1:4:3 has been found. In contrast, the thinnest film (8 Å in the average) showed a drastically different ratio, being approximately 3:1:1:1:1:3. Thus the spontaneous magnetization changed to a preferential orientation along the normal to the surface. This is a clear evidence of the existence of surface anisotropy. Probably the surface anisotropy depends on the crystallographic orientation, the flatness of the surface, the nature of the coating material... Measurements on well defined surfaces as a function of thickness and also as a function of external fields will be necessary for a deeper understanding of surface anisotropy.

For a study of Ni surfaces, the author's group prepared thin Ni films including 5% 57Fe, sandwiched between MgF2 layers. The Mössbauer spectra are reproduced in figure 3.

Fig. 3: Mössbauer absorption spectra for the MgF2-coated thin films of Ni (5% 57Fe), a) 48 Å-film at 300 K - b) 48 Å-film at 4.2 K - c) 16 Å-film at 300 K - d) 16 Å-film at 300 K with 7 kOe - e) 16 Å-film at 4.2 K.

In the case of a 48 Å film, the absorption lines are sharp and the hyperfine field is equal to the bulk value, 263 kOe at 300 K and 285 kOe at 4.2 K. The intensity ratio is close to 3:4:1:1:4:3. In the case of a 16 Å-film, a considerable fraction of Fe is close to the surface and the 57Fe nuclei act as probes to surface anomalies, if any, such as dead layers or antiferromagnetic surface states. The spectrum at 4.2 K however is rather sharp and the hyperfine field is the same as the bulk within the experimental error. Surface anomaly could not be detected. The magnetic moment of Fe at the Ni-MgF2 interface seems to be nearly the same as that in bulk Ni metal.

At 300 K, the 16 Å-film behaves superparamagnetically. When an external field (7 kOe) was applied longitudinally, an effective hyperfine field of about 220 kOe was induced. Therefore the intrinsic Curie temperature is much higher than 300 K. The temperature dependence of thin film magnetization is only partially measurable.

Surfaces of non-metallic compounds were studied by using ultrafine particles. The surface anisotropy due to the coating by organic substances was discussed in the case of NiFe2O4 fine particles. It was claimed that the surface spin is canting in the case of γ-Fe2O3 fine particles.

2.4. Conversion electron spectroscopy. Recently, conversion electron Mössbauer measurements in a backscattering geometry are popularly used. This method is certainly suitable for corrosion and catalysis studies. A gas-flow type counter for this purpose is commercially available. The depth of the observation, however, extends over some 100 Å, which is too large to catch surface phenomena just near the top surface layer. Magnetic behaviors on non-magnetic substances may be detected by using surface-enriched samples. The sensitivity was assured to be high enough for the detection of monolayers.

Depth selective measurements were attempted by using β-spectrometers to analyse the energy of electrons. It was assumed that the energy loss of the conversion electron is proportional to the escape length, i.e. the depth from the surface. The resolution in thickness is in the order of 50 Å, which is not yet sufficient to observe magnetic surface anomalies.

The detection systems for conversion electrons are in progress, for example, Massenet and Daver succeeded to measure at liquid helium temperature using a channeltron. The combination of surface-enriched samples with improved detection techniques...
will be one possibility to study clean vacuum surfaces.

3. Remarks.- The advantages of Mössbauer spectroscopy in the investigation of surface magnetism will be summarized as follows;

(1) Surfaces and also interfaces of bulk crystals can be studied.

(2) Standard values of bulk crystals are well known.

(3) The orientation of the spins are determined by the relative intensity ratio of the hyperfine pattern.

(4) The chemical state of surface atoms is indicated by the spectra. The contamination by O, also by C or by N is distinguishable 36,37/.

Disadvantages are: the number of nuclear species is limited and Mössbauer measurements need relatively long times, therefore, it is difficult to keep a metallic surface clean.

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