

Magnetic Properties of Several Iron Compounds Studied by the Mössbauer Effect

Toshio TAKADA, Masao KIYAMA, Yoshichika BANDO
and Teruya SHINJO*

Received June 25, 1969

Iron oxides, hydroxides and oxyhydrates were prepared as precipitates from aqueous solutions and their properties were studied by the Mössbauer effect and other means. Results are concisely summarized in a table.

Taking advantage of the samples prepared from aqueous solutions, the following two studies were carried out. The one is the particle size dependence of the Mössbauer spectra. The occurrence of the superparamagnetism was confirmed in the spectrum of ultra fine particles. The other is a utilization of oriented particles. Making use of the anisotropic particle shape, oriented samples were produced and spin directions of iron oxyhydrates were estimated.

I. INTRODUCTION

It was in 1958 that Mössbauer reported the discovery of the recoilless nuclear absorption and radiation of gamma ray (the Mössbauer effect). Since then, the effect has been applied rapidly for various investigations in extensive fields of physics and chemistry.¹⁾ The values of isomer shift, quadrupole interaction, magnetic hyperfine interaction and other quantities which are obtained from the Mössbauer spectroscopy are very useful for the microscopic study of electrons' situation.²⁾ A great fortunate for investigators of solid state, especially of magnetism, is the fact that Fe⁵⁷ is one of the best Mössbauer nuclei. While the effect originally belonged to nuclear physics, solid state application is now much dominant. Above all, Fe⁵⁷ Mössbauer measurement is regarded to be an indispensable tool for every kind of research of iron compounds or alloys.

For more than ten years, the authors (T. T. and M. K.) have studied the chemistry of ferrous and ferric solutions and succeeded to clarify the preparation condition of various iron compounds which were produced as precipitates from the solutions. It was fully examined by uncountable practices how the precipitates are affected by temperature, pH, concentration or other factors. Stimulation of experimental data was made possible not only to prepare single phase samples but also to controll the particle size. As described in this article, many fruitful results were obtained by applying the Mössbauer effect to these samples.

Until very recently, the magnetic properties of iron hydrates or oxyhydrates were not made clear. The reason was partially because of sample's deficiency and partially because of their unusual features. For instance, β -FeOOH showed

* 高田 利夫, 木山 雅雄, 坂東 尚周, 新庄 輝也: Laboratory of Solid State Chemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto.

temperature independent susceptibility between 300°K and 4°K (26×10^{-6} CGSemu/g) and therefore the existence of the magnetic order could not be confirmed. Using the samples of high purity and sufficiently large particle size to exclude the size effects, the authors have clarified the physical properties of those compounds by the Mössbauer effect and other means as summarized in the table of Sec. III (a). Here, the Fe⁵⁷ Mössbauer effect was proved to be very powerful for the research of such materials.

The iron compounds prepared from aqueous solutions are also obtained as natural minerals and some of them can be produced by a ceramic method. Samples of precipitates from aqueous solutions, however, have some characteristics which are advantageous for investigators, that are, (1) purity, (2) particle size and (3) particle shape.

In order to study the intrinsic properties of the material, the sample must have a high purity. Generally the purity of carefully synthesized samples is much higher than that of natural minerals.

In contrast with samples produced by other methods, precipitates in aqueous solution consist of individually isolated particles. Each of them is a single crystal having the same particle shape and a similar particle size. By the control of the atmosphere of the sample preparation, it is possible to make particles of different sizes. Therefore the samples of precipitated particles are suitable for the study of the particle size dependence of various physical properties. As an example, Mössbauer observation of the superparamagnetism will be introduced in Sec. III (b).

When the particle shape is anisotropic, samples of preferred oriented particles can be produced. Utilizing the oriented samples as the absorbers of the Mössbauer effect, the spin directions of α -, β - and γ -FeOOH in antiferromagnetic states were estimated as described in Sec III (c). Another example of utilization of oriented samples was the study of Ni(OH)₂ which was reported a few years ago.³⁾ There was shown the oriented sample to be effective as well as a single crystal sample for the investigation of the magnetism and the magnetic anisotropy.

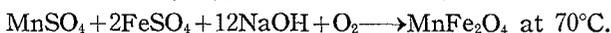
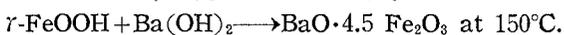
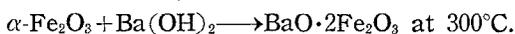
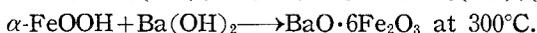
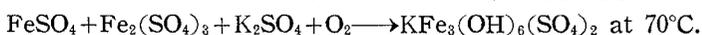
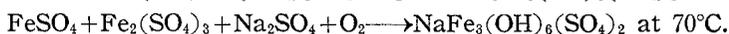
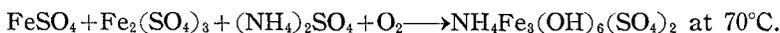
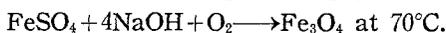
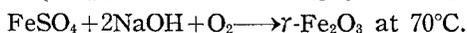
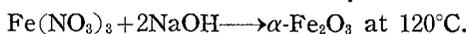
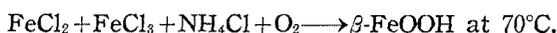
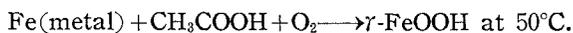
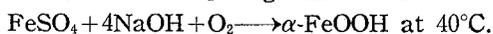
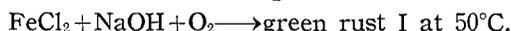
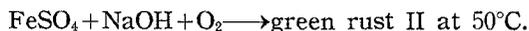
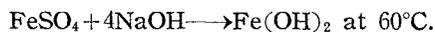
Although the chemical composition is the same, some materials prepared from aqueous solution show different properties from those of ceramic samples. An example included in the table of Sec. III is the case of MnFe₂O₄. The origin is due to the difference of cation distribution to A and B site of the spinel structure.

The distribution of Fe atoms was determined by the Mössbauer effect under an external field and that of Mn atoms could be estimated by nuclear magnetic resonance study also under an external field.⁴⁾

II. EXPERIMENTAL

Because a concise expression of preparation method of each compound is impossible, only the chemical formulas of sample preparation are written in the present paper. The diagrammatic expression of the preparation condition of the whole system will be introduced by Kiyama in near future. The samples were prepared according to the following chemical formulas. All are the reactions in

aqueous solutions and O₂ means bubbling air gas.



Samples were examined by x-ray diffraction, chemical analysis, infrared absorption and electron microscope. Particle size was estimated by direct observation of electron microscope, the broadening of the x-ray diffraction pattern or gas absorption method. The observed values listed in the table of the next section are due to the samples of large particle size (except Fe(OH)₂ and BaO·4.5Fe₂O₃, the diameter of particle is larger than 1 μ).

Mössbauer effect measurements were carried out by commercial TMC apparatus. Magnetic susceptibility was measured by using a torsion balance magnetometer or AC Hartshorn method.

III. RESULTS AND DISCUSSION

(a) Properties of the iron compounds

In Table 1. the experimental results are listed with their mineralogical names and crystallographical constants. The color of the particle considerably depends on the particle size. Written here are the representative colors. Except BaO·4.5Fe₂O₃ and BaO·2Fe₂O₃, the determination of the crystal structures was already made by former investigators and therefore the values cited here are not original ones of the present study.

Listed values of IS in the table are observed shifts at room temperature. In order to derive the intrinsic value of isomer shift, the temperature dependent, second Doppler shift must be eliminated from the observed shift. It is, however, easy to distinguish the valence state of Fe, ferric or ferrous, from the observed shift and therefore Mössbauer effect is useful for the quantitative analysis of iron in ionic compounds.

Among the ferric compounds, the difference of isomer shift is not large. The discussion about the small difference of the shift is very difficult at the present

Several Iron Compounds Studies by the Mossbauer Effect

Table 1. The name of materials, colors of the particles, crystal structures, lattice constants, particle shapes, magnetic transition temperatures (T_N), internal fields at 0°K(Hi(0)), isomer shifts against pure iron (IS) and spin directions at

Formula	Name	Color	Crystal structure	a ₀ (A)	b ₀ (A)	c ₀ (A)
				Lattice constant		
Fe(OH) ₂ ⁽⁵⁾	ferrous hydroxide	white	hexagonal	3.262,	4.596	
FeSO ₄ ·3Fe(OH) ₂	white rust	grayish white	hexagonal	3.174,	10.94	
α-FeOOH ⁽⁶⁾	goethite	yellowish brown	orthorombic	4.587,	9.937,	3.015
β-FeOOH ⁽⁶⁾		dull orange yellow	tetragonal	10.48,	3.06	
γ-FeOOH	lepidrocrite	dull orange	orthorombic	3.87,	12.51,	3.06
Fe ₃ O ₄ ^(a)	magnetite	black	cubic	8.396		
γ-Fe ₂ O ₃ ^(a)	maghemite	brownish red	cubic	8.338		
α-Fe ₂ O ₃ ^(a)	hematite	dark red	hexagonal	5.035,	13.75	
^(b)	green rust I	dark blue green	hexagonal	3.18 ~3.23,	22.5 ~24.2	
FeOOH·Fe(OH) ₂	green rust II	dark green	hexagonal	3.174,	10.94	
NaFe ₃ (OH) ₆ (SO ₄) ₂ ⁽⁷⁾	jarosite	amber yellow	hexagonal	4.18,	16.3	
NH ₄ Fe ₃ (OH) ₆ (SO ₄) ₂ ⁽⁷⁾				4.20,	17.0	
KFe ₃ (OH) ₆ (SO ₄) ₂ ⁽⁷⁾				4.20,	17.0	
MnFe ₂ O ₄ ⁽⁴⁾	manganese ferrite	brown	cubic	8.50		
BaO·6Fe ₂ O ₃ ^(a)	barium ferrite	brown	hexagonal	5.88	23.17	
BaO·4.5Fe ₂ O ₃			hexagonal	4.8	11.4	
BaO·2Fe ₂ O ₃			hexagonal	5.12	13.75	

Remarks :

(a) Because there have been many publications concerning the magnetic and Mössbauer results on these compounds, the citation of the references is abbreviated here. No difference was found between the ceramic samples and aqueous ones, concerning these materials.

(b) A compound consisting of Fe²⁺, Fe³⁺, O, OH and halogens. The ratio of Fe²⁺/Fe³⁺ is about 2. This compound seems to have a rather wide composition range.

(c) Determined from the temperature dependence of the magnetic susceptibility.

(d) Determined from the temperature dependence of the internal field.

(e) Extrapolated value from the temperature dependence of the internal field at Mn⁵⁵ observed by NMR. This value is much higher than that of a ceramic sample.

(f) Fe₃O₄ has a transition at about 120°K. Both above and below the transition tem-

stage. However, the difference of magnetic ordering temperature makes the distinctive contrast between the spectra of each ferric compound. Therefore, the quantitative analysis of the chemical phases in a sample is possible by the Mössbauer measurement of the internal field. The magnitude of the internal field is supposed to be a useful information on the state of chemical bonding, which is more sensitive than the isomer shift but the quantitative discussion is not yet possible. The internal field seems to be reduced by a covalent bonding.

(b) Superparamagnetism

ordered states. (AF), (F) and (PF) mean the type of order to be antiferromagnetic, ferrimagnetic and parasitic ferromagnetic.

Particle shape	T_N	Hi(O)	IS	Spin direction
hexagonal flake	34°K ^(e) (AF)	200kOe	1.2mm/sec	c-plane ^(h)
hexagonal plate	400°K ^(d) (AF)			
needle	9°K ^(e) (AF)	530	0.5	c-axis ⁽ⁱ⁾
needle	270°K ^(d) (AF)	490	0.5	c-axis ⁽ⁱ⁾
plate	50°K ^(e) (AF)	470	0.5	c-axis ⁽ⁱ⁾
cube	848°K (F)	^(f)	^(f)	<111>
cube	856°K (F)	515	0.4	<111>
hexagonal plate	956°K (PF)	530	0.36	c-plane (<258°K) c-axis (>258°K)
hexagonal plate	~4°K ^(e) (AF)			
hexagonal plate	7.5°K ^(e) (AF)		0.4 1.4	
hexagonal plate	53°K ^(e) (AF)	470	0.4	
	55°K ^(e) (AF)	480	0.4	
	60°K ^(e) (AF)	470	0.4	
cube	770°K ^(e) (AF)	510	0.5	
hexagonal plate	720°K (F)	^(g)	^(g)	c-axis
sphere	~300°K ^(d) (AF)			
hexagonal plate	620°K ^(e) (PF?)	{540 510	0.4	

perature, two kinds of Fe are observed in the Mössbauer spectrum. Internal fields (isomer shifts) are 470 kOe (0.8 mm/sec) and 495 kOe (0.4 mm/sec) at 300°K and 470 kOe (0.8 mm/sec) and 510 kOe (0.5 mm/sec) at 80°K.

(g) Four kinds of Fe are included in this compound. Internal fields at 300°K are (1) 415 kOe, (2) 485 kOe, (3) 510 kOe and (4) 580 kOe. Isomer shifts are 0.4 mm/sec for (1), (2) and (3) and 0.3 mm/sec for (4). At 0°K, internal fields of (1), (2) and (3) tend to be 550 kOe and that of (4) is about 620 kOe.

(h) Determined from the analysis of the relation between the internal field and electric field gradient.

(i) Determined from the experimental result using the sample of oriented particles (see Sec III (c)).

Mössbauer absorption spectra of magnetically ordered samples usually show the magnetic hyperfine splittings. The magnetic hyperfine field (or internal field) is mainly caused by unpaired electrons surrounding the nucleus and the temperature dependence is proportional to the sublattice magnetization. An observation of the internal field is the most reliable evidence for the existence of a magnetic order and from its temperature dependence, the Néel temperature can be determined.

In case of ultra fine particles, the situation is quite different. The magnetization of the particle fluctuates rapidly by the thermal agitation. This phenomenon

is called the superparamagnetism. According to Néel's discussion, the relaxation time of superparamagnetism can be expressed by the following relation,⁸⁾

$$\tau = \frac{1}{f_0} \exp\left(\frac{KV}{kT}\right)$$

where f_0 is a temperature insensitive constant with order of $10^9 \sim 10^{10}$ c/sec. K is the effective anisotropy constant and V is the particle volume. Here the anisotropy is assumed to be uniaxial and therefore KV means the potential barrier separating two easy axes. If not uniaxial, a certain factor must be multiplied. With decrease of the particle size and with increase of the temperature, the flipping of the magnetization should become faster.

On the other hand, in order to observe the internal field by the Mössbauer effect, the electron spin (or the magnetization of the particle) must be stable in a longer time than the nuclear Larmor precession time, which is the order of 10^{-8} sec in iron compounds. When the particle size becomes smaller and the relaxation time of the superparamagnetism becomes shorter than the critical value, the Mössbauer spectrum will be paramagnetic. Because the observation time of the Mössbauer effect is thus very short, the dynamical behavior of the magnetic

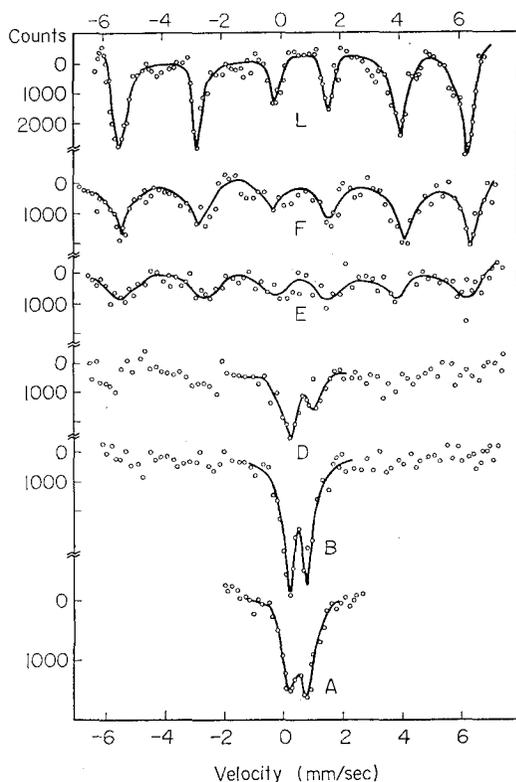


Fig. 1. Mössbauer absorption spectra of α -FeOOH of various particle sizes at 294°K. The estimated volumes are 3×10^{-18} , 7×10^{-18} , 2×10^{-17} , 5×10^{-17} and 2×10^{-16} cm^3 for Sample A, B, D, E and F respectively. Sample L is larger than 10^{-15} cm^3 .

properties of ultra fine particles can be studied. In cases of other, steady experimental methods, the critical time for superparamagnetism, τ_c , is 10^{0-2} sec, which is much longer than the case of Mössbauer effect.

Samples of α -FeOOH of various particle sizes and of narrow size distribution are prepared for the Mössbauer effect observation as a function of particle size.⁹⁾ Figure 1 is the result measured at room temperature. Because the Néel temperature is higher than room temperature, the sample of large crystal size shows the spectrum of distinctive 6-line splitting whose internal field is 365 kOe. The spectrum of the smallest particles (sample A) is however completely paramagnetic and only the quadrupole splitting is appreciable. This fact indicates that the relaxation time of sample A is much shorter than the nuclear Larmor precession time. From this result, the critical volume where the collapse of the internal field begins is found to be about 3×10^{-17} cm³ at 294°K.

Inserting this value into the equation (1) and assuming f_0 is 10^{10} , and $\tau = 2 \times 10^{-8}$ sec, the effective anisotropy constant turns out to be 10^4 erg/cm³. There is no torque measurement to examine this result but the order of this value seems to be reasonable.

According to the results of theoretical calculations where the distribution can be neglected, the Mössbauer effect is able to determine the fluctuation rate of the electron spin in the range of 10^{-7} to 10^{-11} sec.¹⁰⁾ The Mössbauer effect seems to be a useful method to determine the particle size in ultra fine particle region where the other methods give no reliable values and especially the Mössbauer effect will furnish a valuable information concerning the distribution of the particle size.¹¹⁾

(c) Measurement of oriented particles

In general, the spin direction of a magnetically ordered sample can not be determined by the Mössbauer spectra as far as a powder sample is used. An exceptional case is such that an electric quadrupole interaction coexists with the magnetic hyperfine field and the property of electric field gradient is able to be determined. By analyzing the positions of the Mössbauer absorption lines, the angle between the direction of internal magnetic field and the electric field gradient can be derived. The spin direction of antiferromagnetic Fe(OH)₂ was elucidated by this method.⁵⁾

Another case where the spin direction can be estimated is the utilization of samples of oriented particles. The principle is essentially the same as the single crystal experiment. As already described, the particles prepared from aqueous solutions are individually isolated having the same particle shape. If the shape is anisotropic, to give the orientation will be possible.

The particle shapes of oxyhydrates are acicular and seem to be suitable to make the oriented samples. The longest axis of the particles is known to be crystal c-axis from the study of electron microscope. The measurements on the oriented samples of α -, β - and γ -FeOOH in antiferromagnetic states were carried out for the purpose to estimate the spin direction.⁶⁾

The orientation was given as follow: The particles well suspended in water were filtered very slowly through the Membran filter and after drying, they were

pressed with uniaxial pressure of 10^3 kg/cm².

By x-ray diffraction, it was confirmed that there was a strong tendency that crystal c-axis was laid down on the sample plane but the other directions were nearly at random. Mössbauer measurements on the oriented samples were carried out without removing the filter and therefore the crystal c-axis must be in perpendicular to the gamma ray direction. Randomly oriented samples were also measured for comparison, which were prepared with the powders mixed with silicon grease.

The Mössbauer spectra of α -FeOOH at room temperature are shown in Fig. 2. The peak positions are the same between random and oriented samples giving the magnetic hyperfine field of 365 kOe. On the other hand, the intensity ratio of six absorption peaks is varied greatly by the orientation. If the angle between the magnetic hyperfine field direction and gamma ray beam is θ , the angular dependence of Mössbauer probabilities can be expressed as $9/4 (1 + \cos^2\theta)$ for peak 1 and 6, $3 \cos^2\theta$ for peak 2 and 5 and $3/4 (1 + \cos^2\theta)$ for peak 3 and 4, here the peaks are numbered from the lowest energy.

The quadrupole interaction can be neglected in the discussion of relative intensity of six peaks, because it is much smaller than the magnetic hyperfine interaction.

When the direction of the magnetic hyperfine field is completely at random, the relative intensity of six peaks is expected to be 3:2:1:1:2:3: as the result of the average over a sphere of angular dependence for each component.

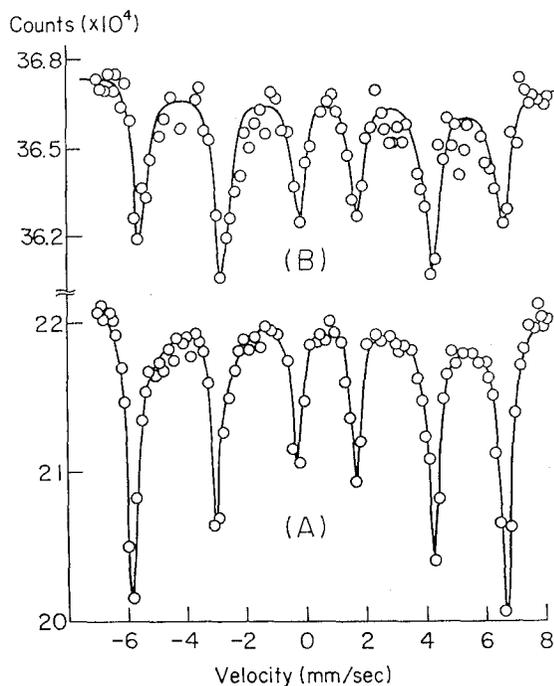


Fig. 2. Mössbauer absorption spectra of α -FeOOH at room temperature.
(A) random sample (B) oriented sample

In case that the magnetic hyperfine field is parallel or perpendicular to the incident gamma ray, the ratio becomes 3:0:1:1:0:3 or 3:4:1:1:4:3. The spectrum of random sample shown in Fig. 2 has the expected intensity ratio of 3:2:1:1:2:3 and therefore it is confirmed that the magnetic spin directions in this sample are ideally at random. The intensity ratio of oriented sample, however, is very close to 3:4:1:1:4:3. Let us assume that the orientation degree is 100 %, namely the c-axis of all particles lies in the sample plane and that the orientation of a- or b- axis is completely at random.

If the easy direction of antiferromagnetic spins is in c-axis, the intensity ratio must be 3:4:1:1:4:3: but if it is in a direction of c-plane, the ratio must be similar with random sample's one. Apparently the former is in good agreement and therefore it is clarified that the antiferromagnetic spins in α -FeOOH are directed collinearly in c-axis.

Similar attempts were made for β -FeOOH at liquid nitrogen and for γ -FeOOH at liquid helium temperature. Spectra of ordered samples are shown in Fig. 3. Obtained results were essentially the same with the present α -FeOOH's one and the spin direction was concluded to be c-axis in each compounds.

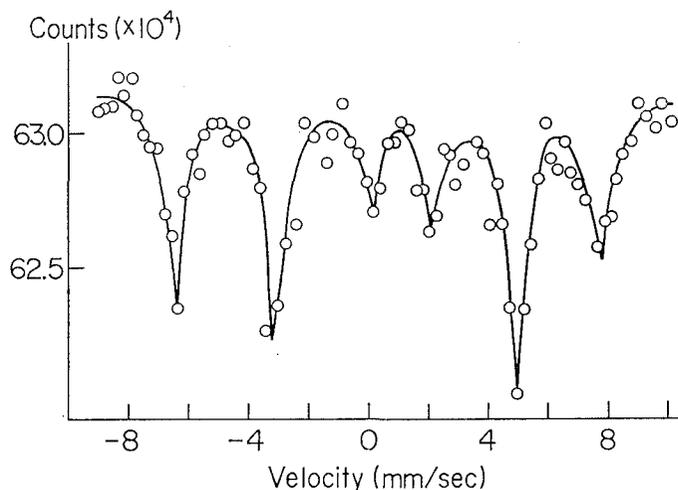


Fig. 3. Mössbauer absorption spectrum of oriented β -FeOOH at liquid nitrogen temperature.

Such experiments are helpful for these compounds because the neutron diffraction technique does not suit for materials containing hydrogen atoms.

Also suggested in the present result is that it is possible to determine the degree of particle orientation by the measurement of Mössbauer lines' intensity.

REFERENCES

- (1) A. H. Muir Jr., K. J. Ando and H. M. Coogan, Mössbauer Effect Data Index, 1958-1965, Interscience Publisher, (1966).
- (2) G. K. Wertheim., Mössbauer Effect; Principles and Its Applications, Academic Press, (1964).

Several Iron Compounds Studies by the Mössbauer Effect

- (3) T. Takada, Y. Bando, M. Kiyama, H. Miyamoto and T. Sato, *J. Phys. Soc. Japan*, **21**, 2745 (1966).
- (4) H. Yasuoka, A. Hirai, T. Shinjo, M. Kiyama, Y. Bando and T. Takada, *J. Phys. Soc. Japan*, **22**, 174 (1967).
- (5) H. Miyamoto, T. Shinjo, Y. Bando and T. Takada, *J. Phys. Soc. Japan*, **23**, 1421 (1967). and *Bull. Ins. Chem. Res. Kyoto Univ.*, **45**, 333 (1967).
- (6) N. Yamamoto, T. Shinjo, M. Kiyama, Y. Bando and T. Takada, *J. Phys. Soc. Japan*, **25**, 1267 (1968).
- (7) M. Takano, T. Shinjo, M. Kiyama and T. Takada, *J. Phys. Soc. Japan*, **25**, 902 (1968).
- (8) L. Néel *Ann. Geophys.*, **5**, 99 (1949).
- (9) T. Shinjo, *J. Phys. Soc. Japan*, **21**, 917 (1966).
- (10) H. H. Wickmann and G. K. Wertheim, *Chemical Application of Mössbauer Spectroscopy* edited by V. I. Gordanskii and R. H. Herber, Academic Press 548 (1968).
- (11) S. Nasu, T. Shinjo, Y. Nakamura and Y. Murakami, *J. Phys. Soc. Japan*, **23**, 664 (1967).