学位申請論文

新庄輝也

MÖSSBAUER EFFECT IN ANTIFERROMAGNETIC FINE PARTICLES

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Mössbauer measurements were made on the fine particles of antiferromagnetic α-FeOOH of various particle sizes to examine the Mössbauer spectra in fluctuating fields.   In the ultra fine samples, the collapse of the internal field due to superparamagnetism was observed.   The critical volume at 294°K was found to be $3 \times 10^{-17} cm^3$ and the critical temperature for the sample of $1 \times 10^{-17} cm^3$ to be 210°K.   The effective anisotropy constant can be estimated to the order of $10^4 erg/cm^3$.   The obtained spectra in the intermediate region between 6-line and 2-line were discussed and the assignment of the doublet in paramagnetic state was attempted in comparison with Blume's prediction.

§ 1. Introduction

A great number of magnetic materials has been investigated by the Mössbauer effect and the magnetic hyperfine field acting on the nucleus (internal field) was observed in various cases[1]. Since the internal field is caused by unpaired electrons surrounding the nucleus, whether the internal field is observable or not by the Mössbauer measurement depends on the relaxation time of the electron spin. To observe the internal field, the relaxation time of the electron spin should be much longer than the nuclear Larmor precession time, which is the order of 10^{-8} sec in the usual iron compounds or alloys.

From the view point of the relaxation time, almost all subjects of the Mössbauer experiments so far can be classified into two groups; the one is magnetically ordered where the relaxation time of the electron spin (magnetization) is infinitely long and the other is paramagnetic where the relaxation time is very short. The observation of the Mössbauer effect under fluctuating fields as a function of relaxation time seems to be of great interest but there have been few works to try to clarify the intermediate situation between the two extremes.

In a previous letter of the author's group[2], the collapse of internal field due to superparamagnetism was reported on a sample of ultra fine α-Fe$_2$O$_3$ (about 50Å in diameter) at 300°K[3]. On the other hand, at 110°K, the spectrum was similar with that of bulk α-Fe$_2$O$_3$. These results show that the relaxation time of

the antiferromagnetic spin in the particle becomes shorter than
the nuclear Larmor precession time between 110°K and 300°K.
Independently of us, the collapse of internal field on
ferrimagnetic fine particles was reported by Schuele et al.[4]
The fine particles, therefore, seems to be suitable materials for
observing the Mössbauer effect in fluctuating fields.

According to Néel's discussion[5], the relaxation time of the
superparamagnetism, τ, can be expressed by the following relation,

$$\tau = (1/fo)\exp(KV/kT) \qquad\qquad (1)$$

where fo is a temperature insensitive constant with approximate
order of 10^{10}c/s, K the effective anisotropy constant and V the
particle volume.   Here, the anisotropy is assumed to be uniaxial
and therefore KV means the potential barrier separating two easy
directions.   This kind of treatment was shown to be reasonable
by the succeeding study of Brown[6] and a refinement for the ultra
fine particle region, KV$<$kT, was carried out by Aharoni[7].
As τ should decrease with increasing temperature and with
decreasing particle size, the systematic measurements as a
function of temperature and particle size were intended.

This paper reports the observation of Mössbauer spectra in
fluctuating fields in antiferromagnetic α-FeOOH with various
particle sizes at various temperatures. α-FeOOH is an
antiferromagnetic material with Néel temperature of about 400°K[8,9]

Since the quadrupole interaction is existing at Fe^{57} nucleus in α-FeOOH, the obtained spectra in the magnetic relaxation can be discussed with Blume's prediction[10] and the assignment of the doublet in paramagnetic state may be possible.

Another fact reported in the previous letter on α-Fe_2O_3 is the particle size dependence of the internal field[3]. It is not clear as yet whether the magnetization or magnetic transition temperature has the particle size dependence or not. Generally, measurements at elevated temperatures give rise to the grain growth of particles but in the present case, the particle size dependence of the internal field may be observed because the Néel temperature of α-FeOOH is not far above the room temperature. A similar trial was made by Lee et al.[11] on ultra thin films of iron and the reduction of Tc and Ms was concluded. The Mössbauer effect is useful tool for the study of magnetism in small systems especially in antiferromagnetic cases.

The next section presents the experimental results for the examination of the samples and the Mössbauer results of various particle sizes at various temperatures. The obtained spectra are discussed in Section 3.

§ 2. Experimental procedures and results

a) Sample confirmation

Samples of α-FeOOH were prepared by the oxidation of ferrous solution as follows;

$$FeSO_4 + 4NaOH + O_2 \longrightarrow \alpha\text{-FeOOH}.$$
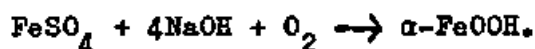
The particle size was controlled by the cation concentration. Obtained samples were examined by X-ray diffraction, electron microscopy and thermal analysis. The particle size estimated straightforwardly from the broadening of the X-ray diffraction peaks are listed in Table 1. Two examples of electron micrograph are shown in Fig. 1. We can see that the particle shape is of needle type and that almost all particles have the same crystal shape. The particle size seems to be satisfactorily uniform. The mean particle volume of the sample was obtained as listed in the table.[*] These values agree with the results obtained from

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[*] Separately, Kiyama will report the method of particle shape determination and the detail of particle volume estimation.

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the gas absorption method (BET method) within the factor of two.

The results of magnetic susceptibility measurements are shown in Fig. 2. With decrease of particle size, the susceptibility increases gradually and the superparamagnetic behavior becomes apparent. The increase of the susceptibility in antiferromagnetic

fine particles is not ~~usual~~ unusual; Néel has accounted for this

phenomenon to be originated from the unballance of the two

magnetic sublattices in the particle.[12] Thus the samples were

proved to be fairly reliable.

b). Mössbauer apparatus and results

Mössbauer effect measurements were made by a conventional

multichannel type apparatus which is the same as the previously

reported one by Nakamura and Shimizu[13] except minor modification.

For the γ-ray source, Co^{57} was electroplated onto a copper plate

and diffused in it. The source was vibrated sinusoidally with

65c/s by an electric vibrator. A NaI scintillation counter was

used as a detecter and 14.4 keV. γ-ray signals selected by a single

channel analyser were fed to a 400 channel pulse height analyser

(TMC) after a time to pulse height conversion with saw tooth mode.

The velocity scale of the obtained spectra was calibrated by the

peak positions of the standard absorbers, Fe and stainless steel

foils.

The temperature control device is as follows; a doughnut

shaped sample holder of copper block was covered by styrofoam

and a small heater and a ring of copper fine pipe were attached on

it. The sample was cooled by liquid nitrogen which was pumped

out through the pipe. The temperature was regulated with the

on-off control of the heater current. The fluctuation of

temperature during the measurement was about 1°K and the absolute

values may have a systematic error within 3°K.   The source was

always at room temperature.

In Fig. 3, the Mössbauer absorption spectra of Sample A, B, D,

E, F and L at 294°K are shown.   The counts accumulated per

each channel were about 7×10^{4} and afterwards the background was

subtracted.   The central parts of the spectra on Sample C at

various temperatures are shown in Fig. 4.   The counts per channel

were about 4×10^{4}

§ 3.   Discussion

From the spectrum of Sample L in Fig. 3, the internal field

at 294°K is evaluated to be 365 kOe.   Rossiter and Hodgson[14]

reported the internal field in α-FeOOH at room temperature to be

364 kOe and v. Ooesterhout[9] got 388 kOe.   According to

Hrynkiewicz et al.[15], however, there are two internal fields in

α-FeOOH and the values are 342 kOe and 283 kOe.   As far as the

present result concerns, almost all Fe belongs to a well resolved

6-line and therefore it seems impossible that this material has

four sublattices.

The feature of the transition from 6-line to 2-line is shown

as the particle size dependence (Fig. 3) and as the temperature

dependence (Fig. 4).   In Fig. 4, only the two middle lines of

the six are shown.   Recently Blume[10] discussed the shape of

Mössbauer spectrum in a fluctuating field and a fixed electric

field gradient.   Although he considered the case of paramagnetic
ion, the situation of superparamagnetic case can be discussed quite
analogously.   The narrowest limit of the absorption lines is
decided by the intrinsic observation time which is the mean life
time of the nuclear excited state (1.4×10^{-7} sec in case of Fe^{57}).
When the relaxation time becomes short and reaches to this extent,
the broadening of the lines occurs.   If it becomes shorter than
the nuclear Larmor precession time, the collapse of the 6-line begins
and finally the spectrum turns out to be purely paramagnetic.
When a fixed electric field gradient is coexisting, however, the
fluctuation of magnetic field has a different effect on the two
components of the quadrupole split-line.   As illustrated in Fig. 5,
the transition from the $1/2$ level of ground state to the $3/2$ level
of excited state, which makes up the one component of the quadrupole
doublet, has a larger splitting in a magnetic field than the
transition from the $1/2$ to the $1/2$ which makes up the other
component.   We may therefore expect to find a particular range of
the relaxation time in which the $1/2$-$1/2$ line is fully narrowed
while the $1/2$-$3/2$ line is still broad.   This asymmetry of the
doublet is not to be averaged out even if the relaxation time has
a distribution to a certain degree.

If the asymmetry is observable, of a great interest is a
comparison of the quadrupole interaction in paramagnetic state
with that in antiferromagnetic state.   Let us consider the simple
case where the electric field gradient is uniaxial.

This approximation is good for most cases because the asymmetric parameter of the field gradient appears as a quadratic term and is usually small. The splitting in paramagnetic state, E, is then given by,

$$|E| = |(1/2)e^2qQ| \qquad (2)$$

where eq is the electric field gradient along the principal axis and Q the nuclear quadrupole moment.

While in the antiferromagnetic state, for the internal field is very large, the quadrupole interaction may appear as a small pertubation of the Zeeman splitting and its magnitude depends on the relative angle, θ, between the internal field and the electric field gradient axis. The quadrupole interaction can be expressed conventionally by the difference of splittings, $S_1 - S_2$, as shown in Fig. 5, when it is not very large. $S_1 - S2$ is represented by the relation,

$$S_1 - S_2 = -(1/2)e^2qQ(3\cos^2\theta - 1). \qquad (3)$$

If the sign of E is known from the asymmetry caused by the magnetic relaxation, we can estimate the angle θ comparing E with $S_1 - S_2$ because e^2qQ should be a common factor in the two equations.

From the experimental results shown in Fig. 3, the critical volume where the collapse of the internal field begins is found to

be about $3 \times 10^{-17} cm^3$ at $294^{\circ}K$. According to the results in Fig.4, the critical temperature for the sample of $1 \times 10^{-17}cm^3$ is obtained to be roughly $210^{\circ}K$. Inserting these values into the equation (1) and assuming $fo = 10^{10}c/s$ and $\tau = 2 \times 10^{-8}sec$, the effective anisotropy constant turns out to be 1×10^4 and 1.5×10^4 erg/cm^3, respectively. There is no torque measurement to examine this result but the order of these values is not unreasonable. The Mössbauer effect seems to be a useful method of particle size estimation in the ultra fine particle region where the other methods give no reliable values. The absolute value of the particle volume is fairly difficult to estimate, because the anisotropy depends complicatedly upon the particle shape and the temperature. But, sometimes, the relatively obtained values by the Mössbauer effect may furnish a valuable information.

Next, let us try to look for the asymmetry and assign the doublet. Although the spectra in the intermediate region between 6-line and 2-line are quite complicated and broadened, it seems natural to choose the lower energy component as due to the $1/2-1/2$ transition, because it is narrower in some cases than the higher energy component. Then we find that qQ is positive in sign. E and $S_1 - S_2$ can be derived as 0.55 ± 0.05 and 0.6 ± 0.1 mm/sec respectively. Using these values, the relation (3) turns out to be $3cos^2\theta - 1 \sim -1$. This conclusion, $cos\theta$ is equal to zero, suggests that the axis of the electric field gradient is perpendicular to the direction of the internal field.

v. Ooesterhout determined the spin direction of α-FeOOH to be in c-axis by the susceptibility measurement on single crystal[9] and therefore the axis of the electric field gradient may lie in the c-plane. The crystal structure was reported already[16,17] but there are still ambiguities in the accuracy of the atomic positions. The estimation of the electric field gradient is rather difficult and no further discussion is possible at present.

As far as the present experiments concern, it is not definite whether the magnitude of the internal field has a particle size dependence or not. According to the results in Fig. 3, the internal field of Sample E and F is approximately the same to the bulk's one in spite of spectrum broadening. For this problem, more accurate and more systematic measurements should be required.

Although our attention was not paid for the particle size dependence of the recoilless fraction and the second order Doppler shift, they might show an unique information on the phonon state in fine particles. Problems of lattice dynamics in fine particles are also attractive for the Mössbauer effect study in future.

Acknowledgements

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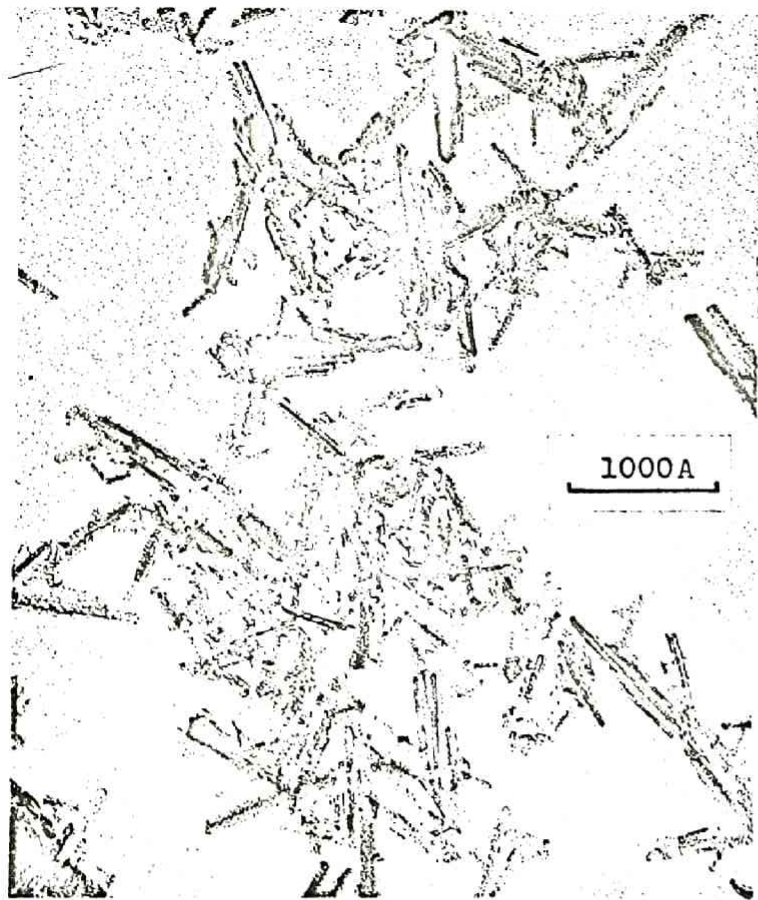14) M. J. Rossiter and A. E. M. Hodgson: J. Inorg. Nucl. Chem. 27 (1   ) 63.

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Table 1.   Particle size of the samples estimated from the broadening
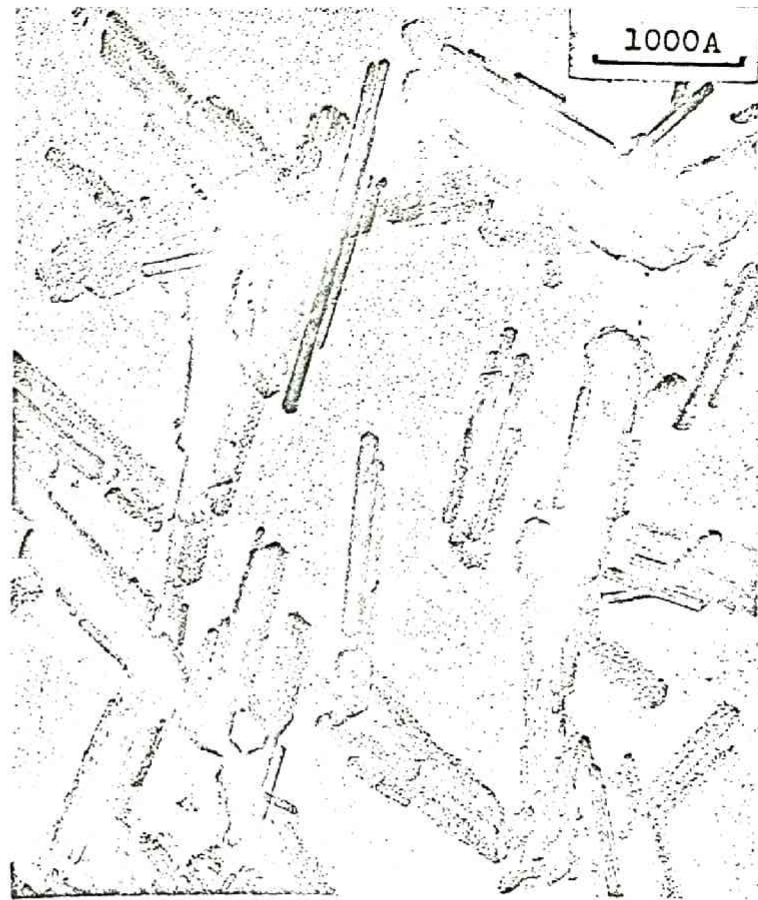   of X-ray diffraction peaks and mean particle volume.

Sample No.	Direction			Volume
	(110)	(130)	(101)	
L(standard)	larger than 10^4A			
G	430A	530	730	3×10^{-15}cm^3
F	240	160	240	2×10^{-16}
E	120	160	160	5×10^{-17}
D	76	74	97	2×10^{-17}
C	70	60	89	1×10^{-17}
B	58	71	64	7×10^{-18}
A	51			3×10^{-18}

Figure captions

Fig. 1.   Electron micrographs of Sample C and F

Fig. 2.   Magnetic susceptibility as a function of temperature

Fig. 3.   Mössbauer absorption spectra of Sample A, B, D, E, F and L
at 294°K.

Fig. 4.   Mössbauer absorption spectra of Sample C as a function of
temperature.   The central parts of the spectra are shown.

Fig. 5   Comparison of the energy schemes in antiferromagnetic and
in superparamagnetic situation.   The spectra to be
expected are illustrated schematically.   Here, τ is the
relaxation time of superparamagnetism and Θ the angle
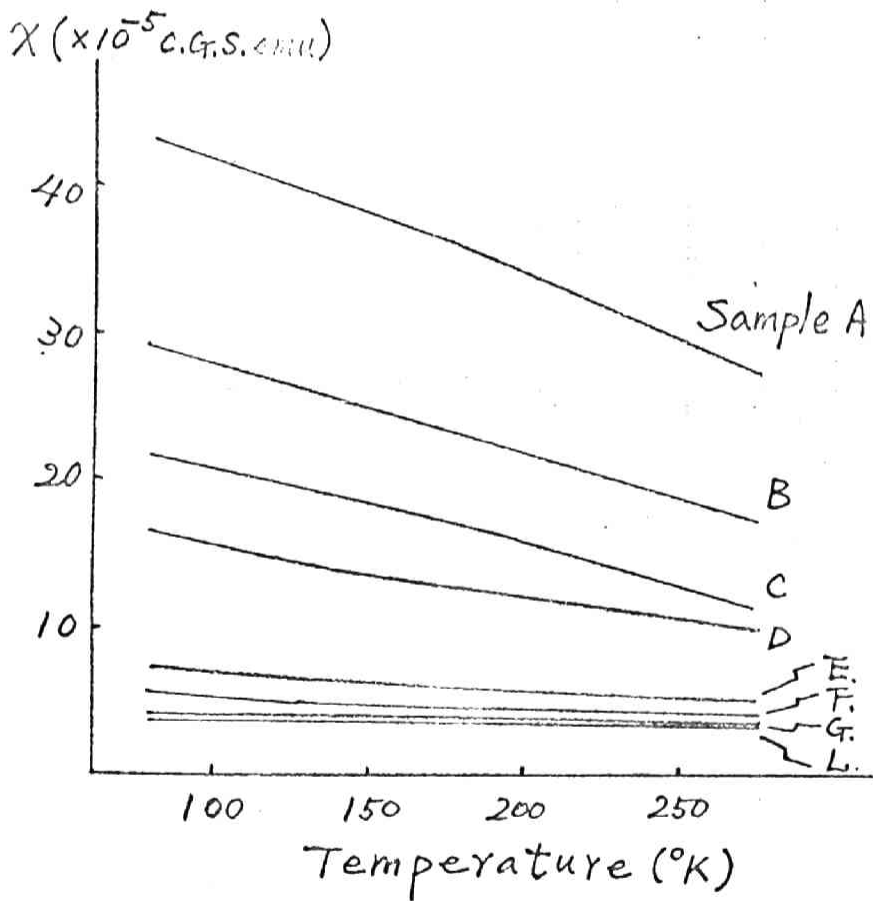between the electric field gradient axis and the internal
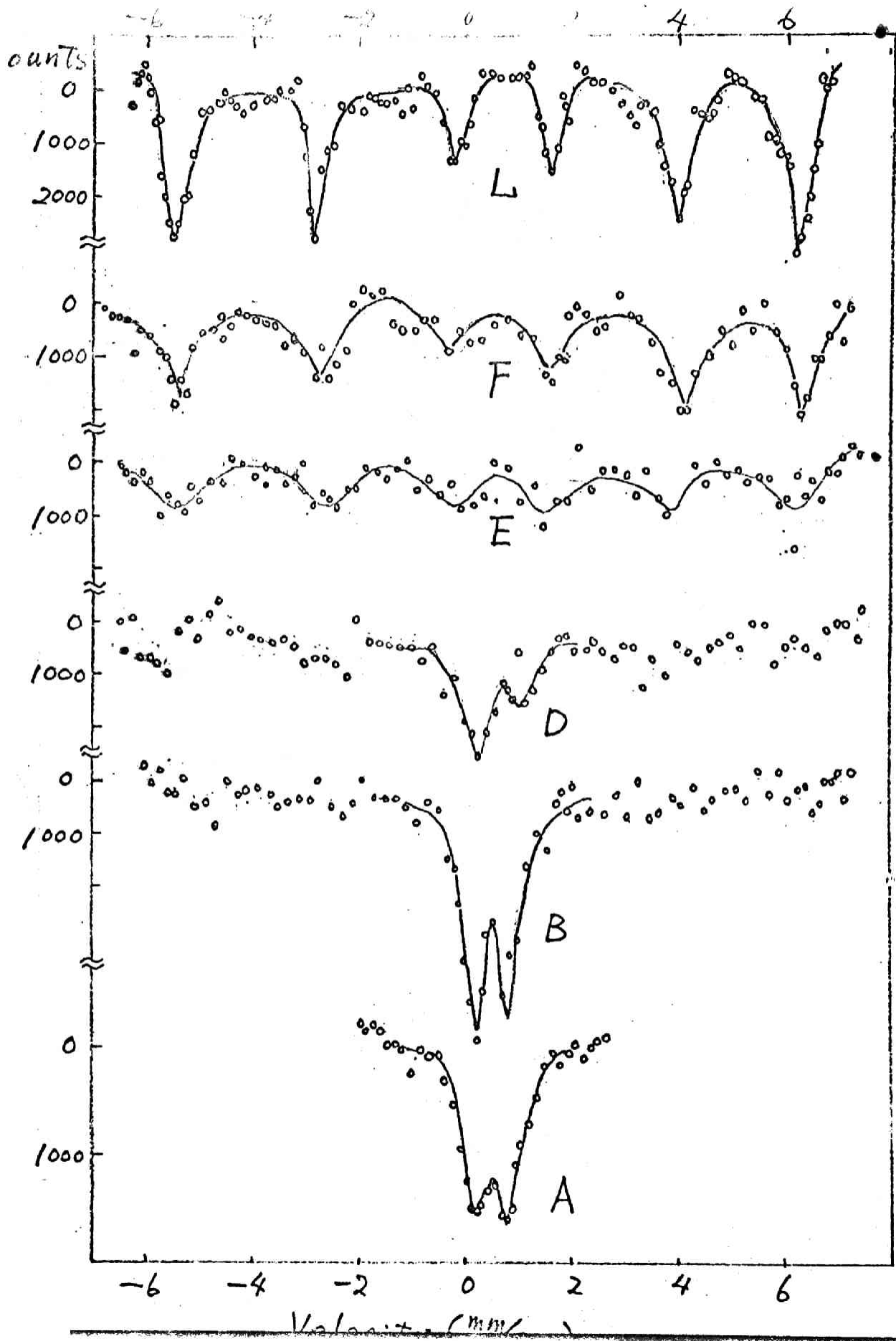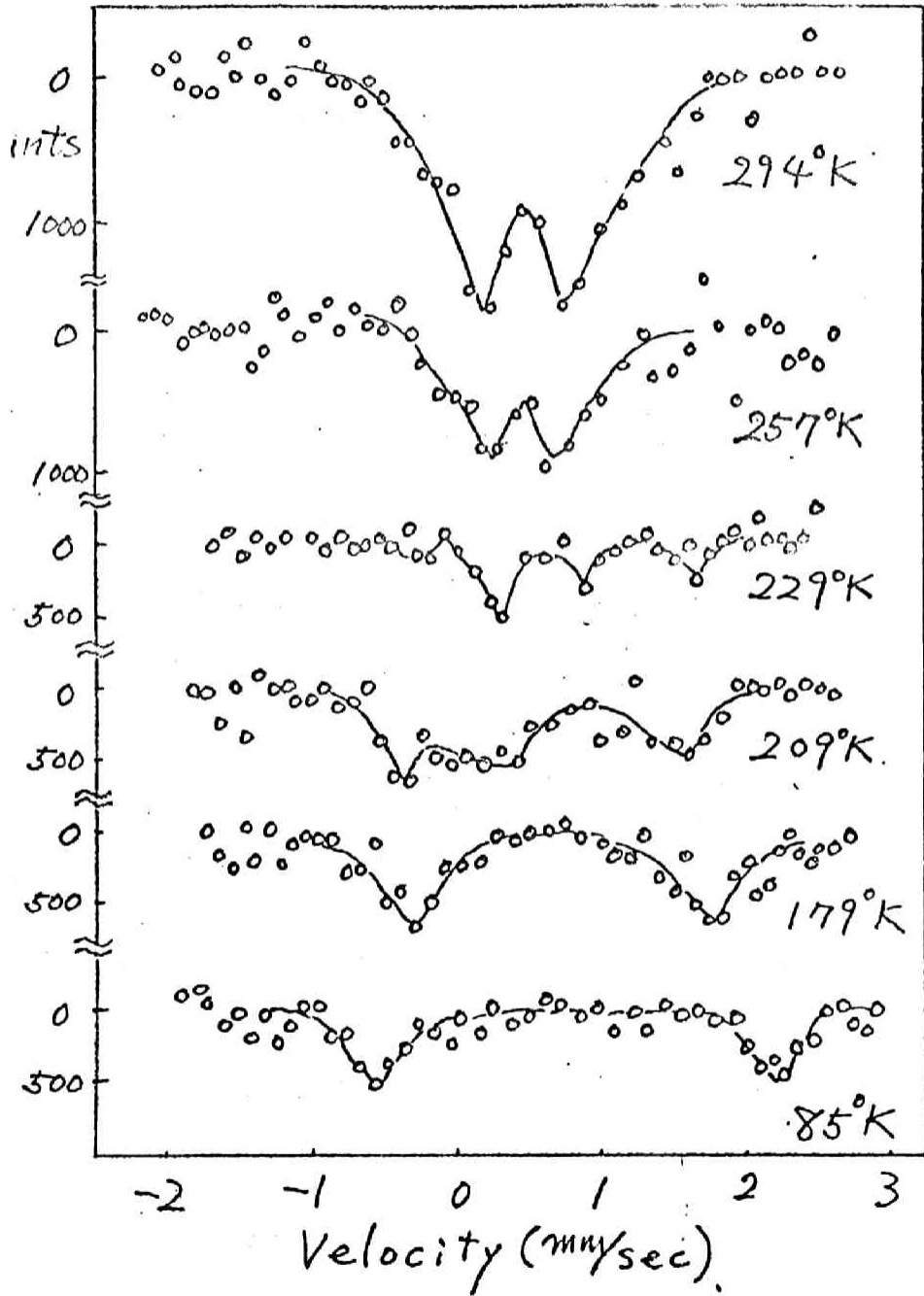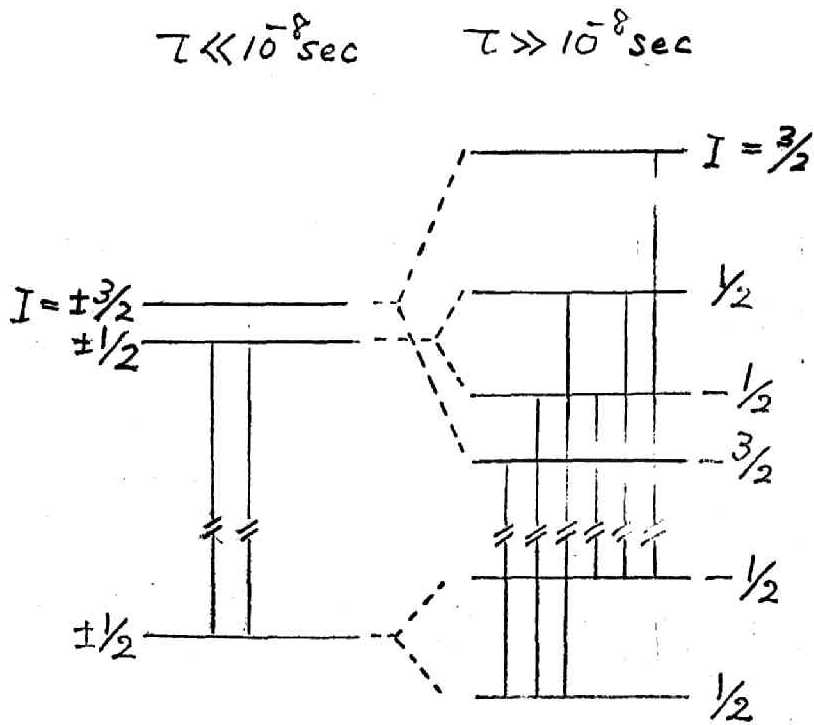field direction.

Sample C

Sample F

Fig. 2.

Fig. 4

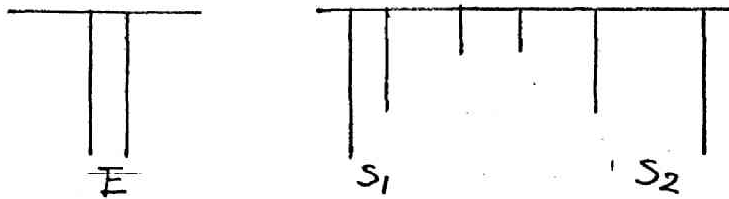Vertical axis label: ints

Temperature labels: 294°K, 257°K, 229°K, 209°K, 179°K, 85°K

X-axis: Velocity (mm/sec)

$$\tau \ll 10^{-8} sec \qquad \tau \gg 10^{-8} sec$$

Fig. 5

$I = \frac{3}{2}$

$I = \pm\frac{3}{2}$
$\pm\frac{1}{2}$

$\frac{1}{2}$

$-\frac{1}{2}$

$-\frac{3}{2}$

$-\frac{1}{2}$

$\pm\frac{1}{2}$

$\frac{1}{2}$

spectrum

E

S_1 S_2

$$|E| = |\tfrac{1}{2} e^2 q Q|$$

$$S_1 - S_2 = -\tfrac{1}{2} e^2 q Q (3\cos^2\theta - 1)$$