Natural Science Report, Ochanomizu University, Vol. 41, No. 1, 1990
お茶の水女子大学 自然科学報告 第41巻 第1号

Detection of a Correlation between the Orientation and the Magnitude of the Hyperfine Field of ^{57}Fe in $YFeMnO_4$

Midori Tanaka, Junji Iida and Hitomi Ohi

Department of Physics, Faculty of Science, Ochanomizu University
Bunkyo-ku, Tokyo 112

Overlapped Mössbauer spectra of a single crystal $YFeMnO_4$ are analyzed using the Hesse method extended to determine the distribution of magnetic two parameters, specifying the orientation and the magnitude of the hyperfine field. A nearly linear correlation between them is detected under the condition of incident γ-rays parallel to the c-axis. It is discussed that a misfit around the center two lines may be attributed to a certain dynamical effect of spin behavior.

§1. Introduction

Mössbauer study on $YFeMnO_4$ gives us various interesting information[1)2)]. One of them is the existence of a correlation between the orientation and the magnitude of the hyperfine field. To obtain this correlation, the Hesse method has been extended.

The Hesse method has been known to be useful to determine a hyperfine field distribution, $p(H)$, for a powder Mössbauer spectrum with an overlapping sextet[3)]. This method is also applicable to the distribution of the magnitude of H with a preferred direction. Actually, there are some examples in spin glass and even in amorphous materials, where not only the $p(H)$ but also the intensity ratio, R, of the second or the fifth lines to the innermost lines[4)] were determined. In the determination, it must be required that all the hyperfine fields have the same orientation-distribution. However this requirement is not always valid for all the cases. An anisotropy axis is generally the most stable direction in the spin system, so that its magnetic energy should differ compared with other axes. For instance, in a case, where an anisotropy energy can not be neglected in a spin system with a competing interaction, the dynamic behaviors of spins would depend on their orientation with respect to the anisotropy axis. The Mössbauer nucleus feels the spin fluctuation as the time averaged hyperfine field. In such a case, if the sample is a single crystal, correlation between the orientation and the magnitude of hyperfine field would appear in the spectrum.

There is a Hesse method extended to the determination of the distribution of any two parameters among the magnetic parameter H_{hf}, and the other four quadrupole parameters, e^2Qq, η, θ, ϕ[5].

In our case, however, the special interest is in the correlation between the magnetic two parameters, specifying the orientation θ to the anisotropy axis and the magnitude H_{hf} of hyperfine field. We have no information about such a correlation, except our present oxide*.

Such a correlation is observed in the narrow temperature range between 50 and 60 K for ^{57}Fe in $YFeMnO_4$.

We need to introduce characteristic features of this oxide. $YFeMnO_4$ has been known as a Heisenberg-like spin system in the antiferromagnet on a triangular lattice. The temperature 60 K is the point where a cusp-like peak is observed in the magnetization measurement ($H//c$-axis, $H=50$ Oe)[6], and a broad magnetic spectrum begins to be observed in the Mössbauer measurement[1]. The spectrum indicates not only the very wide distribution of H_{hf} but also a preference of hyperfine fields to the c-axis. In the temperature range $80\,\mathrm{K}<T<150\,\mathrm{K}$, the spectra are similar to but slightly different from the paramagnetic quadrupole doublet at 300 K. At least in the Mössbauer time scale, the spins are in a paramagnetic-like state. In the neutron diffraction measurements, however, the spin-correlation is observed below 200 K[7]. Such a temperature range is very wide compared to those in other two-dimensional competing systems. On the other hand, below 45 K, the anomalously wide distributions disappear. In the both cases of $\gamma//c$-axis and $\gamma//c$-plane at 4.2 K, the line widths are very narrow and the intensity ratios are the same as that of the powder spectrum. These phenomena reflect the anomalous features of this frustrated system, and not incompatible with the model of the Heisenberg spin system on a triangular lattice in an antiferromagnet[8].

In this report, the experimental results and the analysis in the temperature range between 50 and 60 K will be shown in detail.

§ 2. Experimental

Mössbauer spectra were detected for three species A, B and C: A is a platelet of the single crystal cut in the c-plane, B is that cut in the a-c plane, or in the plane parallel to the c-axis. Each thickness is about 60 μm. C is the polycrystalline sample crushed from a part of the same rod as the single crystal. Hereafter, each spectrum is called A, B or C, respectively.

* The procedure of a bi-parameter distribution analysis by R. E. Vandenberghe et al. is similar to ours. It has been reported in the ICAME 1989 (Budapest) in the same section with ours. They have applied it to the Mössbauer spectra with external magnetic fields.

The spectrometer is a conventional constant acceleration spectrometer in a usual transmission arrangement. Velocity was calibrated with a Fe metal absorber. Temperatures were controlled within an accuracy of 0.1 K in the range between 4.2 K and 300 K.

The paramagnetic spectrum at 300 K shows a quadrupole doublet with the splitting (from peak to peak) of 0.52 mm/s and the full widths of half maximum (FWHM), Γ, of 0.4 mm/s. The spectrum at 4.2 K is a well resolved sextet with narrow widths, of about 0.4 mm/s for the innermost lines and about 0.6 mm/s for the outermost. The spectra A, B are almost the same as C in position and intensity, and are symmetric to the center. As an example, the spectra at 4.2 K and 300 K for A are shown in Fig. 1. The temperature dependences of those spectra are shown in Figs. 2(a), (b) and (c).

It is noticed that the spectral shape shows marked changes in the hyperfine field distribution and the intensity ratios in the temperature range between 50 K and 60 K. The

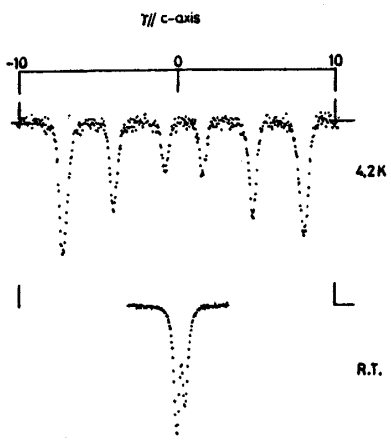


Fig. 1. Mössbauer spectra for the single crystal A ($\gamma//c$-axis) of $YFeMnO_4$: the hyperfine sextet at 4.2 K, and the quadrupole doublet at 300 K.

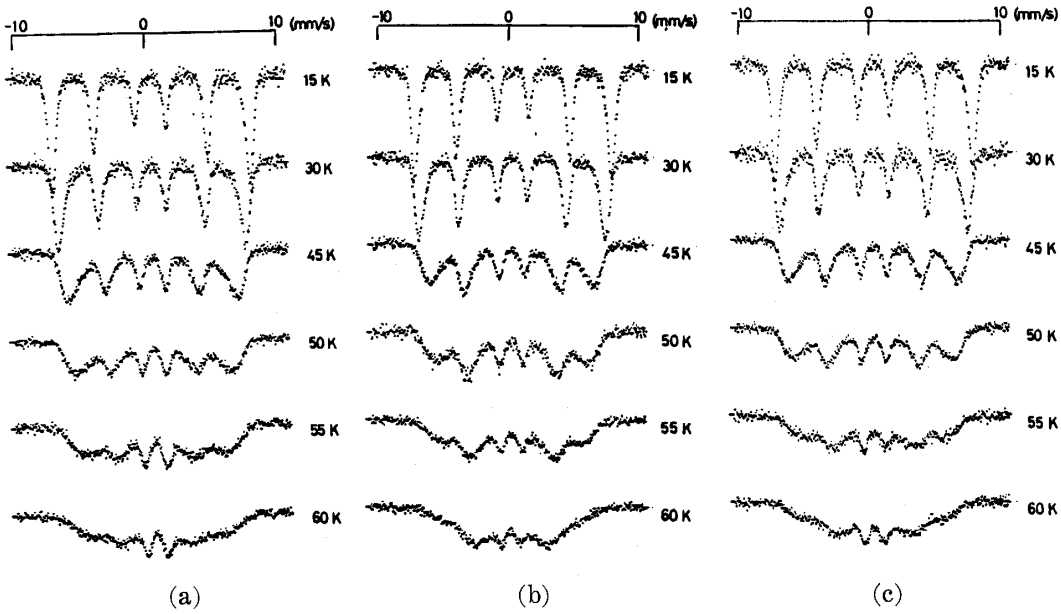


Fig. 2. Temperature dependence of Mössbauer spectra of $YFeMnO_4$: (a) for A ($\gamma//c$-axis); (b) for B ($\gamma\perp c$-axis); (c) for C (powder sample).

analysis of these spectra is the main object in this report.

§ 3. Analysis and Results

a) *Method for the determination of two parameter-distribution.*

The theoretical spectrum can be written as follows:

$$Y_{\text{theor}}(V)=\iint P(\theta, H)\, Y_{\text{cal}}(\theta, H, V)\, d\theta dH\,,$$

where $P(\theta, H)$ is a two-dimensional distribution function of two parameters, θ and H. θ is the angle between the hyperfine field and the incident γ-rays, and H is the magnitude of the hyperfine field. $Y_{\text{cal}}(\theta, H, V)$ is a line shape function written as follows. V means the Doppler velocity in Mössbauer effect.

$$Y_{\text{cal}}(\theta, H, V)=BG-\Sigma_I\ \text{Int}(\theta, I)L(V, I)\,,$$

where BG represents a back ground and I the line number of a sextet. $\text{Int}(\theta, I)$ is a intensity function and $L(V, I)$ is a Lorentzian shape function.

$$L(V, I)=(\Gamma/2)^2/((V-V_0(H, I))^2+(\Gamma/2)^2)\,,$$

where $V_0(H, I)$ is a function of the I-th line position. In the present case, the quadrupole interaction can be neglected, because the spectra are symmetric to the center in position and intensity, so that the intensity function can be written as follows:

$$\text{Int}(\theta, I)=3(1+\cos^2\theta) \quad \text{for } I=1, 6$$

$$\text{Int}(\theta, I)=4\sin^2\theta \quad \text{for } I=2, 5$$

$$\text{Int}(\theta, I)=1+\cos^2\theta \quad \text{for } I=3, 4.$$

$P(\theta, H)$ is determined according to the least square fitting method:

$$\int[Y_{\text{theo}}(V)-Y_{\text{obs}}(V)]^2 dV=\text{minimum},$$

where $Y_{\text{obs}}(V)$ means the observed spectral intensity. We call this method the 2D-Hesse method. In the case of no correlation, $P(\theta, H)$ can be separated into $p(\theta)$ and $p(H)$, and the determination of R is possible using the usual Hesse method.

b) *Selection of parameters*

The analysis by the 2D-Hesse method was performed in three temperature points, 50 K, 55 K and 60 K. In this temperature range, the region of H_{hf} from 30 kOe to 450 kOe was selected through the analysis of the powder spectra by the usual Hesse method. Smaller hyperfine fields were cut to avoid a spurious fitting because of the non-zero quadrupole

interaction. The region of the angle θ is from 0° to 90°. These two parameters were divided into 22 and 7 sections with each width, $\Delta H_{hf}=$ 20 kOe and $\Delta\theta=15$ degree, respectively, for the reason of a limit in the memory size of the computer. If the width of the field division, ΔH_{hf}, is less than 10 kOe, we can use as a line width the experimental value of 0.4 mm/s determined from the analysis of the paramagnetic spectrum, of which the line width is mainly due to the distribution in the quadrupole splitting. On the condition of $\Delta H_{hf}=20$ kOe, we have to use a larger value of 0.6 mm/s. This was confirmed by fitting the powder spectra using the usual Hesse method with the H-division into 22 sections.

c) *The analytical results*

Good agreements between data and fitting curves can be seen in Figs. 3(a) and (b) for A and B, respectively, except the center lines. Fig. 3(c) is given for C, for the sake of comparison. In these figures, negative values of $P(\theta, H)$ with no physical meaning have been replaced with zero, and then the fitting curves have been recalculated.

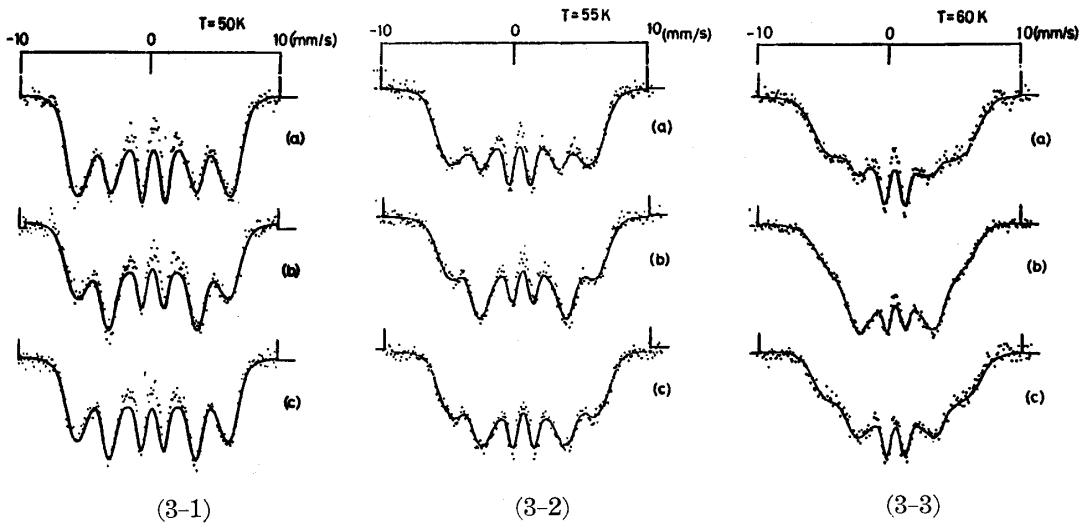
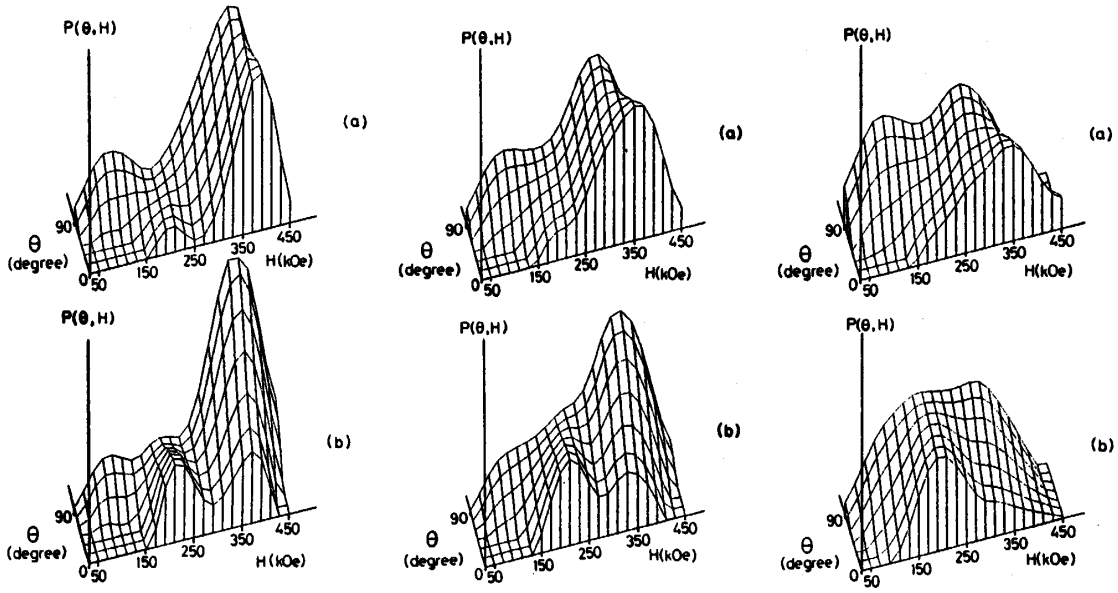


Fig. 3. The best fit curves with experimental results at 50 K (3-1), 55 K (3-2) and 60 K (3-3) using 2D-Hesse method with H_{hf} =20 kOe and Γ=0.6 mm/s: (a) for A; (b) for B; (c) for C.

The results of $P(\theta, H)$ are shown in Figs. 4(a) and (b) for A and B; here $P(\theta, H)$ is not a usual distribution-density with the weight $\sin\theta$, but is proportional to a number of spins having an angle θ. We must direct our attension to the peak of distribution in higher fields than 250 kOe, because the peak in lower fields is attributed to a certain dynamical effect of the spin behavior as discussed later.

A nearly linear relation of the correlation is observed between θ and H, as shown by $P(\theta, H)$ on a θ-H plane in Fig. 5. At 50 K, it is only in



(4-1) (4-2) (4-3)

Fig. 4. Two dimensional distribution $P(\theta, H)$ at 50 K (4-1), 55 K (4-2) and 60 K (4-3), here, θ is the angle of the hyperfine field to the c-axis (the anisotropy axis) and H is the magnitude of the hyperfine field: (a) for A and (b) for B.

the narrow region 350 kOe $< H_{hf} <$ 390 kOe. At 60 K, it is uncertain which shows the maximum of the distribution, since the distributions have plateau shapes. Thus the correlation is most clearly seen at 55 K.

From the very nature of the case, such a correlation is not observed for B.

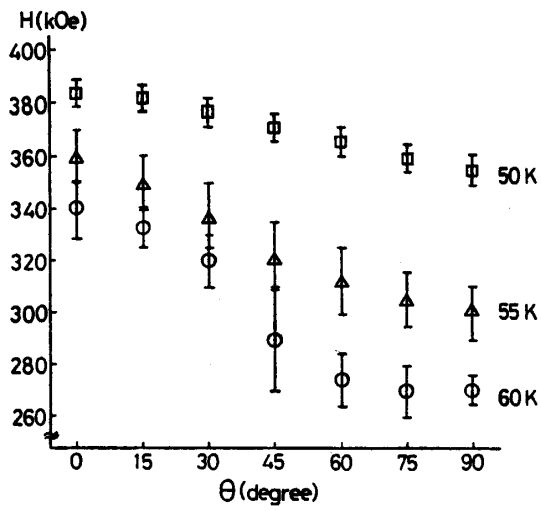


Fig. 5. The correlation between θ and H: (□) for 50 K; (△) for 55 K; (○) for 60 K.

§ 4. Discussion

Existence of the correlation can be confirmed also in the usual Hesse fitting for A (the 1D-Hesse method with $\Delta H_{hf}=10$ kOe, $\Gamma=0.4$ mm/s): First, we determine the distribution of $p(H)$ for powder spectra C with $R=2$. Next, with fixed $p(H)$, the least square method is performed in order to obtain the optimum R value for the single crystal spectrum. Through this procedure, a spurious fitting can be avoided. We can find clear misfits as described later.

Obtained R represents the best fit value within a limit of such a procedure, and is useful to know the characteristics of this material. Not only $p(H)$ but also R drastically change with increasing temperature above 50 K, as shown in Figs. 6 and 7. These phenomena are very anomalous.

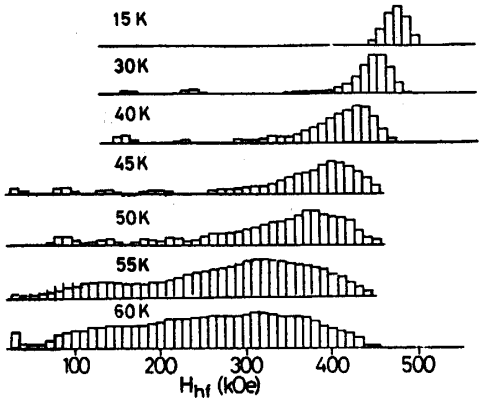


Fig. 6. Temperature variations of the hyperfine field distribution, $p(H)$ in 1D-Hesse method, for powder spectra.

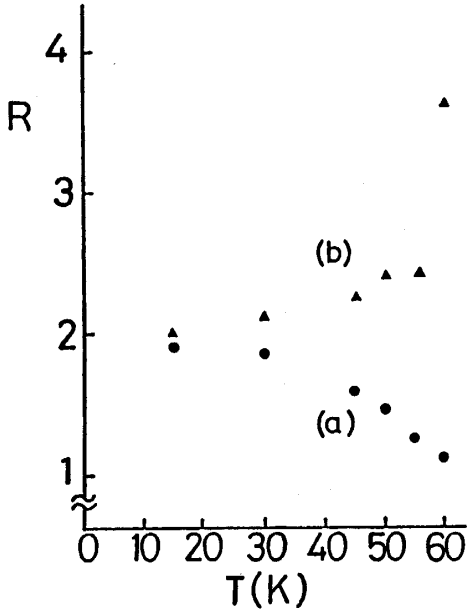


Fig. 7. Temperature variations of the intensity ratio, R, of the second (or the fifth) line determined in 1D-Hesse method: (a) for A and (b) for B.

As shown in Fig. 8(a), this fitting curve for A does not show so good agreement as those of the 2D-Hesse method. The very difference is in the shapes of the second and the fifth lines. The misfit in the both lines represents the tendency that higher fields incline to the c-axis rather than lower ones do. As references, the fitting curves for B and C are also shown in the figure.

The other difference is in the center part: Their absorptions are weaker and their two lines are sharper than the fitting curves. This is not a misfit arising from neglecting the non-zero quadrupole interaction. If a dynamical effect of the

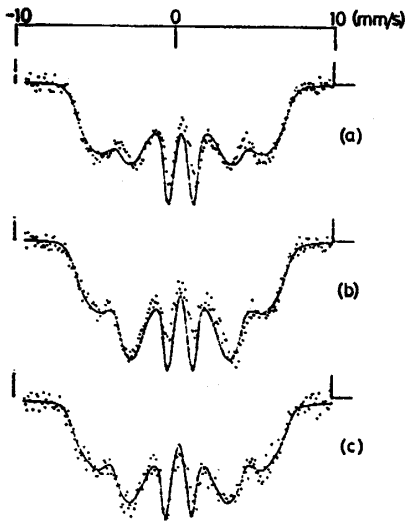


Fig. 8. Fitting curves at 55 K using the 1D-Hesse methhd with $H_{hf}=10$ kOe and $\Gamma=0.4$ mm/s: under the restriction of assuming the same hyperfine field distribution with the powder one; (a) for A with $R=1.24$; (b) for B with $R=2.4$; (c) for C with $R=2.0$.

spin fluctuation was introduced, the calculated center lines should become narrower than outer lines[9], and the center absorptions should become weaker, because the superposition of the second and the fifth lines to the center part must decrease. Such an analysis, however, would become more complex. Now we assume the static model with the same width for every line in the fitting.

Unless the above mentioned restriction on $p(H)$ is imposed, the spectrum is fitted with different $p(H)$. Fig. 9 is a result of the unrestricted fitting for A with $R=1.12$ at 60 K. The agreement is the best of all, including the restricted 1D-Hesse and the 2D-Hesse methods. The $p(H)$, however, has another peak at about 100 kOe for any R value. This means that the correlation in A is substituted with a spurious distribution over small field values. Note the similar result in $p(H)$ at 55 K shown in Fig. 6. It is the problem that even in the powder spectrum, the H-distribution has two peaks. Fitting curves based on this $p(H)$ represent the center two lines with very strong absorptions compared to the data as shown in both of Figs. 8(a) and (b). The peak of the $p(H)$ in the low fields is considered to be spurious. It would suggest another effect than the correlation, probably a certain dynamical effect. The anomalously wide distribution of $p(H)$ at 60 K can be considered to reflect the dynamical spin behavior.

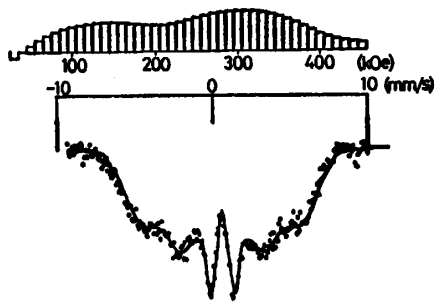


Fig. 9. The best fit results at 60 K using the unrestricted 1D-Hesse method for A with $R=1.12$.

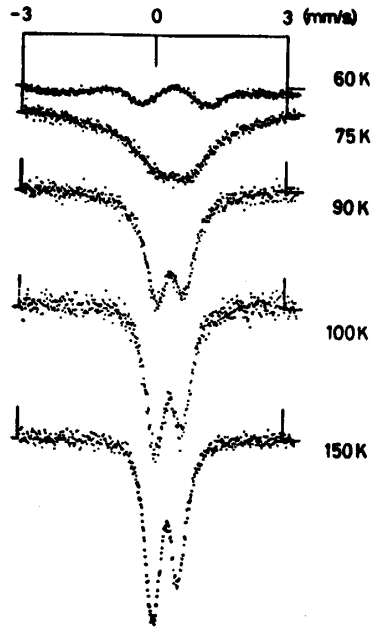


Fig. 10. Temperature variations of the spectra for A in the velocity range -3 mm/s$<V<3$ mm/s and the temperature range 60 K$<T<$300 K. The spectra are different from the paramagnetic doublet at room temperature, and there is no coexistence of a paramagnetic doublet at 60 K.

We add a remark that no coexistence of a paramagnetic doublet is observed below 60 K**. The va-

** In the sintered powder sample of $YFeMnO_4$ reported in reference 1), coexistence of a paramagnetic doublet was observed down to 35 K. It is suggested that the sample was not homogeneous.

riations of the spectra from paramagnetic state to ordered one can be seen in Fig. 10.

The spin dynamics in $YFeMnO_4$ is of very interest. Physical considerations for this oxide will be reported elsewhere.

Acknowledgements

The authors would like to express their thanks to Professor N. Hashitsume for kindly help with respect to the numerical calculation using the IBM computer of Ochanomizu University. The authors deeply appreciate Professors Y. Nakagawa and K. Siratori for valuable discussions in developing the study on this kind of oxide.

References

[1] M. Tanaka, K. Siratori and N. Kimizuka: J. Phys. Soc. Jpn., **53**, 4113 (1984).
[2] M. Tanaka, J. Iida and K. Siratori: International Conference on the Applications of the Mössbauer Effect 2.78b 4-8 September 1989 in Budapest.
[3] J. Hesse and A. Roubartsh: J. Phys., **7E**, 525 (1974).
[4] Y. Takeda, S. Morimoto, A. Ito, T. Sato and Y. Miyako: J. Phys. Soc. Jpn., **54**, 2000 (1985).
H. Wakabayashi, T. Goto, K. Fukamichi, H. Komatsu, S. Morimoto and A. Ito: J. Phys. Soc. Jpn., **58**, 3383 (1989).
[5] N. Hashitsume and H. Komatsu: Nat. Sci. Rep. on the Ochanomizu University **40**, 1 (19t9).
[6] J. Iida et al: In preparation.
[7] K. Siratori, S. Miura, S. Funahashi, J. Akimitsu, N. Kimizuka and S. Takekawa: J. Magn. & Mat., **31-34**, 799 (1983).
[8] H. Kawamura and S. Miyashita: J. Phys. Soc. Jpn., **53**, 9 (1984).
[9] M. Blume and J. A. Tjon: Phys. Rev., **165**, 446 (1968).