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Mössbauer Experiments in External Magnetic Fields

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A strong magnetic field produced by a superconducting magnet is very useful for Mössbauer spectroscopic investigations. The following results were obtained utilizing the high field Mössbauer technique.

(1) Impurity Fe in γ-Mn has no localized magnetic moment. (2) The transferred hyperfine magnetic field at Fe in ferromagnetic CoS_2 was determined. (3) The ion distribution in the manganese ferrite prepared by a wet method was estimated and the spin arrangement was confirmed to be collinear. (4) An unusual behavior was observed in the field dependence of vivianite, $Fe_3(PO_4)_2$-$8H_2O$; only one of the two Fe sites showed a spin flipping phenomenon.

INTRODUCTION

A superconducting magnet has enabled us to make various measurements easily in high magnetic fields. For the Mössbauer spectroscopy also, the high magnetic field is very useful and remarkable advances have been made by utilizing it. Merits of an external high magnetic field for the Mössbauer effect study may be briefly surveyed as the following.

It is well known that the magnetic hyperfine field (internal field) is easily observed in a magnetically ordered state and the magnitude of the internal field at absolute zero is an important key for the study of the electronic structure. The internal field corresponds to the spin density at the nucleus and is delicately affected by the surroundings. When the magnetic ordering temperature is very low, however, the estimation of the internal field is impossible without some ultralow temperature devices. In such cases, a paramagnetic saturation method is useful. A paramagnetic spin will be considerably polarized by the application of high magnetic field at liquid helium temperature region. For instance, the internal field of Fe^{6+} ion in $SrFeO_4$ was estimated to be -140 kOe, although the Néel temperature is below 2°K.[1] The internal field of paramagnetic spin is estimated from the difference between the applied magnetic field and the observed, effective field. Frankel *et al.*[2] have measaured the Mössbauer effect of impurity Fe in Cu applying high magnetic fields up to 136 kOe. They have succeeded in observing the destruction process of the bound state by magnetic fields. This experiment gives an evidence for the existence of the spin compensated state. The impurity states of Fe in various metals were systematically studied by Kitchens *et al.*[3] and it was shown that the Mössbauer effect is very useful for the magnetic study of impurity state in metals. As will be described later, it was confirmed that Fe impurity in γ-Mn has no localized magnetic moment.[4]

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The sign of the internal field is determined by the spectra taken in the presence of external magnetic fields. For both paramagnetic and ferromagnetic substances, the application of external field is necessary to determine the sign of the internal field. The leading origin of the magnetic hyperfine interaction is the Fermi contact term and in the case of Fe, the sign is usually negative, that is, the direction of the internal field is antiparallel to the electron spin polarization.

Let us consider next the cases of magnetically ordered substances. When the sign of the internal field is known, the direction of the electron spin can be determined. One example is the measurement on Fe^{57} in CrO_2.[5] Because the solubility of Fe into CrO_2 is very little, other techniques are not able to clarify the effect of Fe-substitution. Mössbauer spectrum of 1% Fe^{57} in CrO_2 showed that the Fe ions were dissolved in CrO_2 and the valence state was trivalent. The sign of the internal field in Fe^{3+} is no doubt negative. When an external field of 45 kOe was applied, the effective internal field was increased. The spin direction of Fe was thus determined to be antiparallel to the ferromagnetic matrix of CrO_2.

When the high field Mössbauer technique is applied to ferrites, the distribution of Fe ions to each sublattice can be determined. Usually the absorptions of Fe^{3+} ions in A- and B- sites are overlapped, since the difference of the internal field is small. An external field can separate the absorptions because the sublattice magnetizations are antiparallel. In Chapter III, a result on a manganese ferrite prepared by a wet method will be introduced. At the same time, it is also clarified whether the electron spin arrangement is collinear or not. The Mössbauer method is suitable for the estimation of the spin canting angle. Chappert and Frankel[6] showed that the magnetic structure of ferrimagnetic $NiFe_2O_4$ is a collinear, Néel type but $NiFe_{0.3}Cr_{1.7}O_4$ has a triangular structure.

If an external field causes a spin flipping, the Mössbauer spectrum can catch it directly. As intruduced in Chap. III(D), an unusual behavior was observed in the result on vivianite, $Fe_3(PO_4)_28H_2O$; only one of the two Fe sites showed a spin flip phenomenon.[7]

In the next chapter, the experimental procedure will be briefly described. The results on Fe impurity in γ-Mn, Fe impurity in CoS_2, a manganese ferrite prepared by a wet method and vivianite single crystal will be introduced in Chap. III.

EXPERIMENTAL

Figure 1 is a schematic drawing of the stainless steel cryostat including a superconducting solenoid, which was produced by Westinghouse for Mössbauer or optical measurements. The superconducting magnet was laid horizontally at the bottom of the cryostat. The maximum field was 50 kOe with the current of 15.8 A and the persistent mode was always adopted for the Mössbauer measurements. The liquid helium consumed for the precooling was about 5. *l*. Using more 5. *l*, the measurement for more than 24 hr was possible with energizing the coil. The inside bore of the solenoid for the sample space was 26 mm in diameter. The sample was contacted to the wall of the bore with thermal joint grease and its temperature was actually the same with that of the liquid helium.

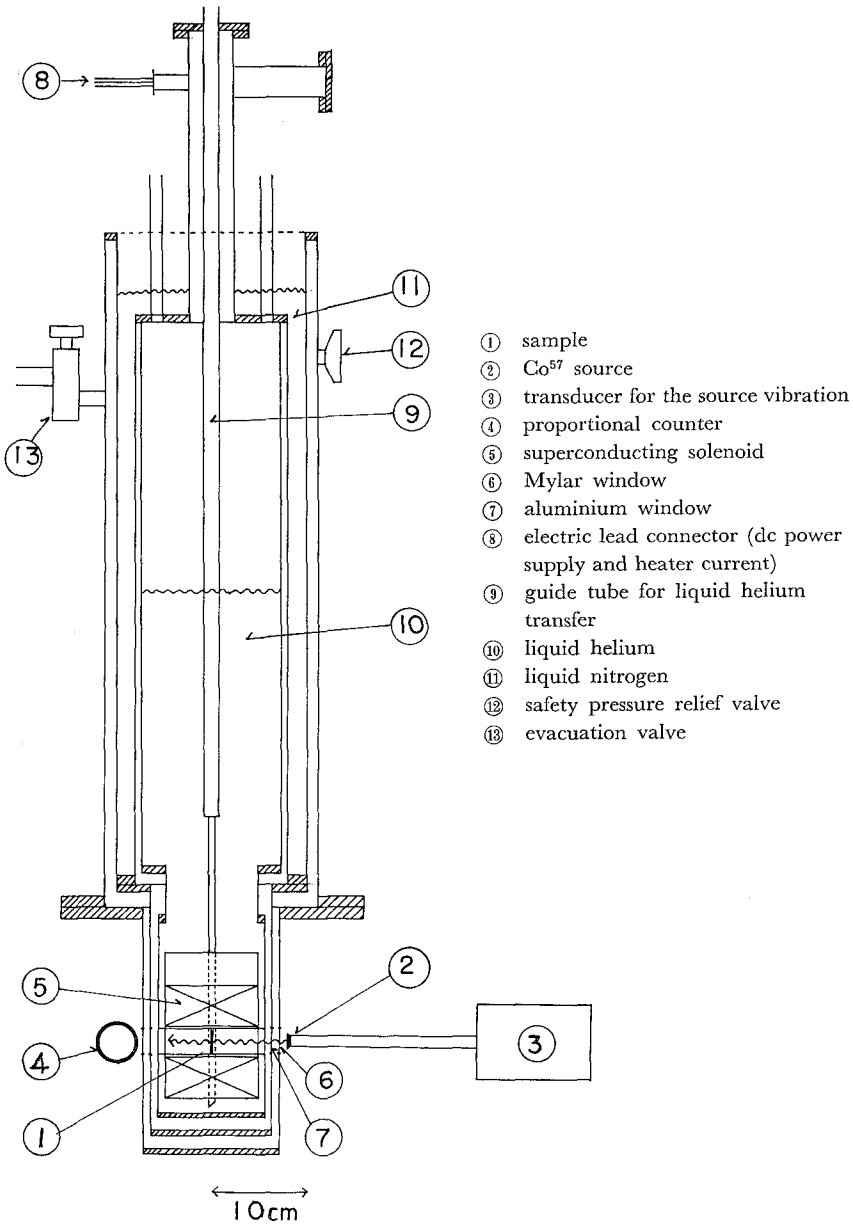

Fig. 1. The illustration of the cryostat including a superconducting magnet.

The gamma ray source was Co^{57} embedded in Cu plate. The source was vibrated parabolically by the Mössbauer Drive Unit 306 of Technical Measurement Corp. The detector was proportional counter, RSG 61 of Reuter-Stokes, in which mixed gas of Kr and CO_2 was sealed. The applied dc voltage for the counter was 1500 V.

The characteristics of the counter were insensitive to the leaked magnetic field. The transducer was separated from the magnet to the distance of 30 cm. When the

magnet was energized up to the maximum, a leaked field of about 3 kOe was observed at the position of the source. For a multiscaller, either a 1024 channel analyzer, Northern Scientific 611, or a 100 channel gammascope, Technical Measurement Corp. model 102, was used.

The Mössbauer sample of γ-Mn containing impurity Fe was prepared by Dr. Y. Endoh by dissolving 1% Fe^{57} into γ-Mn matrix which included 5% Cu for stabilizing the face centered tetragonal phase. The present Mössbauer measurement was a part of an extensive work on Fe-Mn alloys by Dr. Y. Endoh and Prof. Y. Ishikawa in the Institute for Solid State Physics of University of Tokyo.[9]

The sample of CoS_2 containing 1% Fe^{57} was prepared by Dr. K. Kosuge in Department of Chemistry, by a sintering method.

The method of preparation for manganese ferrite from aqueous solution was reported elsewhere.[10]

The single crystal sample of vivianite was a naturally grown mineral and was furnished by Prof. H. Forstat in Physics Department of Michigan State University.

RESULTS AND DISCUSSION

A) Impurity Fe in antiferromagnetic γ-Mn

Magnetic and electric properties of the binary alloy system, Fe-Mn, have been extensively investigated by Endoh and Ishikawa.[8] Their results suggested that

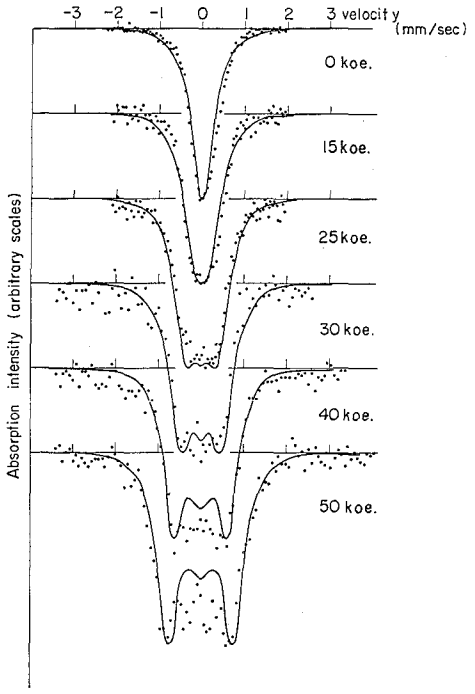

Fig. 2. Mössbauer absorption spectra of $(Mn_{0.99}Fe_{0.01})_{0.95}Cu_{0.05}$ in the presence of various external fields. The temperature of the absorber was always at 4.2°K. The solid lines are calculated ones assuming that the observed field is the same as the external one, *i.e.*, Fe impurity has no electron spin polarization.

impurity Fe in γ-Mn has no localized magnetic moment. On the other hand, Fe atoms in fcc Fe-Mn alloys, where the concentration of Fe is more than 30%, have localized moments of about $1\mu_B$ and internal fields of about 40 kOe. In order to clarify the state of impurity Fe in γ-Mn, the Mössbauer spectra of 1% Fe^{57} in γ-Mn, containing 5% Cu for stabilizing the crystal phase, were taken at 4.2°K in various external fields.

Without external field, the spectrum has no magnetic hyperfine structure, although the Néel temperature of γ-Mn matrix is higher than 200°C. Here are two possibilities; the one is that there is no electron spin polarization at Fe impurity and the other is that Fe behaves paramagnetic although it has a magnetic moment. The field dependence of the spectra indicates that the former is valid because the observed effective field in every case is the same as the externally applied one within the experimental error. The internal field, if exists, is smaller than 5 kOe. It is therefore proved that impurity Fe in γ-Mn has no localized magnetic moment. The disagreement between the observed spectra and the calculated lines may be due to the deviation of intensity ratio from the ideally thin absorber's one, 3 : 0 : 1 : 1 : 0 : 3. The sample was rolled to reduce the thickness but possibly it was not sufficiently thin.

B) Internal field at Fe^{57} in ferromagnetic CoS_2

The disulphide system, $Fe_{1-x}Co_xS_2$, has a cubic phyrite structure in the whole composition range. CoS_2 is ferromagnetic below 120°K having $1\mu_B$ per each Co atom and shows metallic conductivity.[11] On the other hand, FeS_2 has only weak, Pauli paramagnetism. If impurity Fe in ferromagnetic CoS_2 has really no d-spin polarization and if an internal field is observed at Fe^{57}, the origin of the internal field must be the conduction electron polarization. It seems very rare that Fe has no d-moment in a ferromagnetic substance.

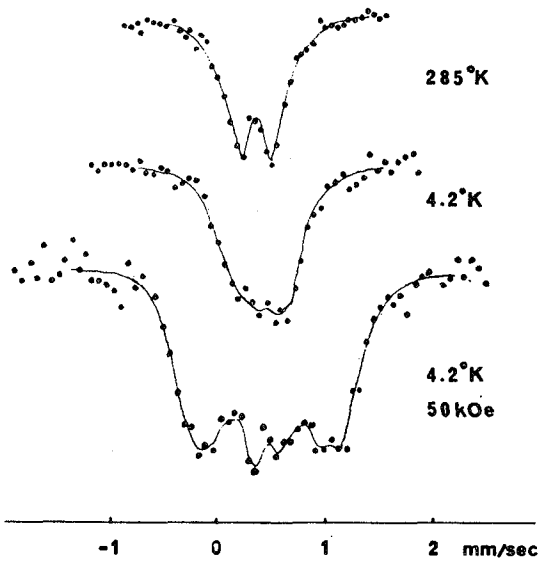

Fig. 3. Mössbauer absorption spectra of Fe^{57} in CoS_2 at 285°K and 4.2°K with and without external field.

The Mössbauer spectra of 1% Fe^{57} in CoS_2 are shown in Fig. 3. The spectrum at 4.2°K without external field has a slight broadening in comparison with the spectrum at 285°K. The fact that the internal field is nearly zero indicates that there is no d-spin polarization at the Fe atom. When an external field of 50 kOe was applied, the effective field was observed to be 41 kOe. No magnetization was additionally induced by the external field. The demagnetizing field is about 1 kOe. Then the internal field is derived to be -8 ± 5 kOe. It is not possible to develop any quantitative analysis from this small value but it is found that the transferred hyperfine field, produced by the conduction electron spin polarization, is very small in this case.

C) Ion distribution in manganese ferrite

The authors have investigated the cation distribution in manganese ferrite prepared as the precipitates in an aqueous solution, by means of NMR,[12] neutron diffraction[13] and x-ray measurement[10] and found that the distribution in a wet ferrite differs greatly from that in a ceramic sample. For the estimation of the site preference of Fe ions, the Mössbauer measurement in the presence of an external field gives the most reliable result. Usually the absorptions due to A- and B-site are overlapped because the difference of the internal field is small. When an external field is applied, the internal field at A-site is increased but that at B-site is shrank because the sublattice magnetizations are antiparallel and the magnetization of B-site is predominant. Then the absorptions are separated and the populations of Fe ions are easily estimated from the intensity ratio of the absorption.

Moreover, the intensity ratio of the six-line shows whether the magnetic structure is collinear or not, which is an important information to study the magnetic properties. If the electron spin is parallel to the gamma ray propagation vector, the absorptions due to $\Delta M=0$ transition must be vanished. If perpendicular, the intensity ratio is 3 : 4 : 1 : 1 : 4 : 3.

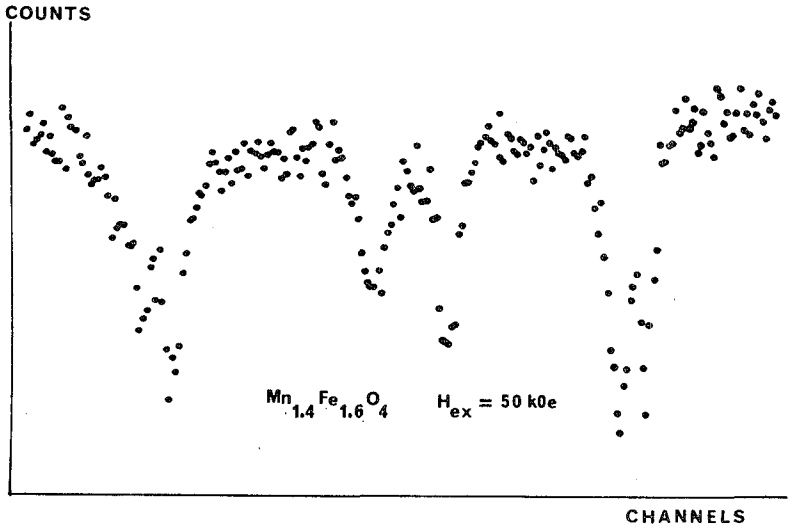

Fig. 4. Mössbauer absorption spectrum of $Mn_{1.4}Fe_{1.6}O_4$ prepared from an aqueous solution, taken at 4.2°K in the presence of external field.

Figure 4 is the spectrum in the presence of 50 kOe of $Mn_{1.4}Fe_{1.6}O_4$ prepared by a wet method. It is well known that more than 90% of A-sites are occupied by Mn ions in case of the manganese ferrite of the same composition prepared by a ceramic method. In contrast, this spectrum shows that a considerable amount of Fe occupy the A-site, which seems more than one third of the total Fe. For both sites, the absorptions due to $\Delta M=0$ transition were vanished. Therefore the spin structure is confirmed to be collinear. The systematic investigation by the Mössbauer effect on the cation distribution in manganese ferrites is in progress.

D) *Spin flipping in vivianite*

The complex magnetic state of vivianite, $Fe_3(PO_4)_2 8H_2O$, has been the subject of many investigations.[14] There are two kinds of Fe site, FeI and FeII, and the Néel temperature is 9°K.

The Mössbauer measurements were carried out at 4.2°K in the presence of external fields to study the spin flip phenomenon. The sample was a single crystal whose ac plane was oriented to be perpendicular to the external field. In this condition, both spin easy axes, at FeI and FeII sites, were perpendicular to the external field. If there is no spin flipping, the field dependence of the spectrum must be very small because the external field is perpendicular to the internal field and the magnitude of the external field is much smaller than the internal one. In fact, the spectrum for FeII site in Fig. 5, shows no field dependence up to 50 kOe.

However, the peak positions of FeI site have greatly shifted with an increase in the external field. The absorptions due to $\Delta M=0$ transition have almost vanished.

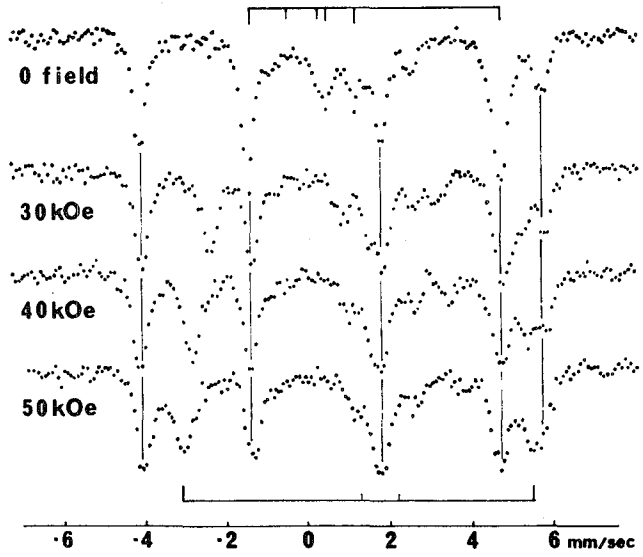

Fig. 5. Mössbauer absorption spectra of vivianite single crystal at 4.2°K with external fields. Longitudinal lines are the main peak positions of FeII, which are nearly independent of the external field. The line positions of FeI at zero and 50 kOe are identified as the stick diagrams illustrated at the top and the bottom of the figure, respectively.

This fact can not be accounted for without assuming a ferromagnetic spin flipping on the FeI site. The spin flipping on one sublattice, independently of the other sublattice is a characteristic of magnetism in vivianite, found in the present experiment. This phenomenon agrees with the crystallographic consideration that the molecular field at FeI is very small.[14] For a quantitative discussion on the spin flip process, it is desirable to compare these results with magnetization measurements under strong magnetic fields.

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