

Mössbauer Effect of FeOCl-Pyridine Complex

F. KANAMARU, M. SHIMADA, AND M. KOIZUMI

The Institute of Scientific and Industrial Research, Osaka University, Osaka 565, Japan

AND

M. TAKANO* AND T. TAKADA

Institute for Chemical Research, Kyoto University

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A Mössbauer effect study has been conducted on FeOCl-pyridine complex in the temperature range between 4.2° and 298°K. The isomer shift relative to Fe metal and the quadrupole splitting at 298°K are 0.36 ± 0.01 and 0.92 ± 0.01 mm/sec, respectively. An antiferromagnetic ordering occurs at $65 \pm 3^\circ\text{K}$. The internal magnetic field is 435 ± 10 kOe at 4.2°K. The z axis of the electric field gradient tensor ($|V_{zz}| > |V_{xx}| \geq |V_{yy}|$, η being small) is shown to be parallel to the direction of the internal magnetic field and perpendicular to the crystalline b axis.

Introduction

In recent years, theoretical and experimental attentions have been given to properties of layer-type compounds (1, 2). This paper describes the Mössbauer effect of a new compound of the above-mentioned type, FeOCl-pyridine complex.

FeOCl belongs to the orthorhombic space group P_{mmm} with 2 FeOCl per unit cell [$a = 3.780$, $b = 7.917$, and $c = 3.302$ Å (3)]. The crystal structure is characterized by the layer-type structure similar to that of γ -FeOOH, which consists of a stack of double layer sheet of oxygen octahedra linked together by shared edges through the nonhydroxyl oxygens. All Fe^{3+} ions are on twofold special positions (b) with point symmetry mm . The outermost atoms on each of the layers are Cl^- ions, and the interlayer Cl^- - Cl^- distance, 3.680 Å, closely approximates twice the van der Waals radius of chlorine. Therefore, FeOCl is expandable with adsorbing a kind of basic organic molecules in the interlayer region.

The Mössbauer effect measurements on FeOCl have been made by several investigators, showing

the compound to be antiferromagnetic below about 90°K (4).¹ The detailed analysis of the magnetic pattern by Grant required two antiferromagnetic sublattices with Fe^{3+} spins||the b axis and||the c axis, respectively. However, this noncolinear magnetic structure is not directly derived from the crystal structure.

In this study, it was found that the magnetic structure of FeOCl was extremely affected by adsorbing pyridine molecules in the interlayer region of FeOCl, which was accompanied with a large expansion of the interlayer distance between the successive sheets of FeOCl.

Experimental

FeOCl was prepared by heating equimolar mixture of FeCl_3 and Fe_2O_3 in an evacuated and sealed Pyrex glass tube at 350°C for 2 weeks followed by slow cooling to room temperature. Thin bladlike crystals ($5 \times 1 \times 0.05$ mm) with the well-developed b plane and with the longest platelet dimension parallel to the c axis were resulted. The X-ray powder diffraction

¹ Kostiner *et al.* (5) observed, by Mössbauer spectroscopy, that FeOCl magnetically ordered below 68°K. However, FeOCl used in this study exhibited the same magnetic behavior as Grant reported.

* Present address: Department of Chemistry, Faculty of Science, Konan University.

pattern of the product agrees with that recorded on ASTM Data Card 1-81.

The reaction with pyridine at 80°C proceeds to a limiting composition containing one pyridine molecule for each three Fe atoms, so that the chemical formula of the resulting compound may be written as $\text{FeOCl}(\text{pyridine})_{1/3}$. This stoichiometry is reflected in both the weight gain and the chemical analysis of the material.

Mössbauer effects on the oriented specimen of FeOCl -pyridine complex so that the b plane was perpendicular to the incident γ -ray beam were measured in the temperature range between 4.2° and 298°K. The γ -ray source, Co^{57} doped in Cu metal, was always kept at room temperature. Calibration of the velocity scale was made by using pure Fe metal and $\alpha\text{-Fe}_2\text{O}_3$ as standard absorbers.

Results and Considerations

The complex produced was black and had the orthorhombic unit cell with $a = 3.78(1)$, $b = 13.45(2)$, and $c = 3.30(1)$ Å. From the comparison of the lattice constants of FeOCl and its pyridine complex, it is deduced that the effect due to adsorption of pyridine molecules is not induced in the double layered sheet of FeOCl but only in the interlayer space. The expansion perpendicular to the b plane approxi-

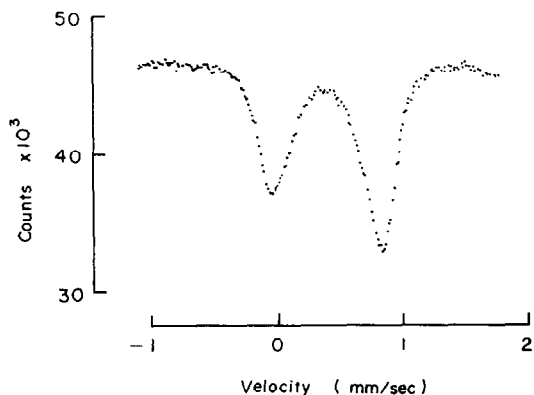


FIG. 2. Mössbauer spectrum of oriented sample of $\text{FeOCl}(\text{pyridine})_{1/3}$ (γ -ray|| b) at room temperature. Velocity scale is relative to Fe-metal.

mately equals that which results in the case when pyridine molecules are placed between the layers having the plane of the molecule perpendicular to the layer, as shown in Fig. 1.

Figure 2 illustrates the room temperature (298°K) Mössbauer spectrum of FeOCl -pyridine complex with the measured values of +0.36(1) mm/sec for the isomer shift, which is typical of a high-spin Fe^{3+} ion, and 0.92(1) mm/sec for the quadrupole splitting (ΔE_Q). The intensity ratio of the higher energy absorption line to the lower one is close to 5/3, the value that is expected

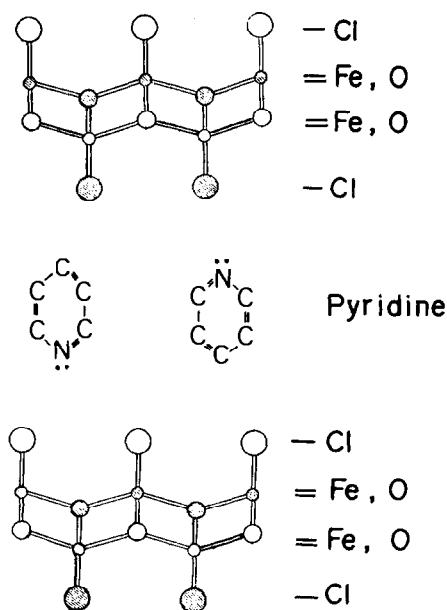


FIG. 1. Schematic representation of a possible structure of $\text{FeOCl}(\text{pyridine})_{1/3}$.

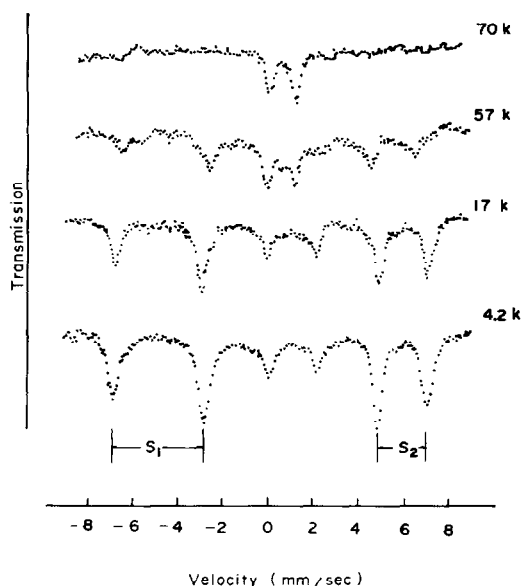


FIG. 3. Mössbauer spectra of oriented sample of $\text{FeOCl}(\text{pyridine})_{1/3}$ (γ -ray|| b) at 4.2°, 17°, 57°, and 70°K. Velocity scale is relative to Fe-metal.

TABLE I

MÖSSBAUER PARAMETERS OF FeOCl(PYRIDINE)_{1/3} AT 298° AND 4.2°K

Temperature (°K)	IS (mm/sec)	QS (mm/sec)	H (kOe)
297	0.36 ± 0.01	0.92 ± 0.01	—
4.2	0.34 ± 0.03	0.93 ± 0.03	448 ± 10

when the principal axis of the electric field gradient (EFG) is perpendicular to the incident γ -ray beam and V_{zz} is negative.

The hyperfine spectrum at 4.2°K consists of only one set of six-line spectrum where the line-width of each absorption line is same within the experimental error. The Mössbauer parameters at 4.2°K are summerized in Table I. The relative intensity ratios of the absorption lines are nearly 3:4:1, indicating that the internal magnetic field (H_{eff}) is oriented perpendicular to the b axis. Since the distance (S_1) between the two lines located at the left side of the pattern is greater than that (S_2) at the right side, as indicated in Fig. 3, the component of the EFG tensor in the direction of H_{eff} is negative. $\Delta S = S_1 - S_2$ is effectively twice the quadrupole splitting in the paramagnetic state, indicating that the internal field is along the z axis of the EFG tensor ($|V_{zz}| > |V_{xx}| \geq |V_{yy}|$, $V_{zz} < 0$, $\eta \approx 0$). In the

case of FeOCl, the EFG parameters are $z \parallel a$, $V_{zz} < 0$, and $\eta = 0.32$ (5-7). If, in FeOCl-pyridine complex too, the z axis is parallel to the a axis, the above-described results indicate that the direction of internal magnetic field is parallel to the a axis. It is reasonable to assume that the electron spin is along the internal magnetic field in an Fe³⁺ ion in high-spin ($S=$) state, because the internal magnetic field arises from the core polarization magnetic hyperfine interaction.

The temperature dependence of the internal magnetic field is shown in Fig. 4. As seen in the figure, H_{eff} versus T curve does not follow a Brillouin function, i.e., H_{eff} decreases almost lineally as the temperature is raised up to 60°K and above 60°K abruptly. The magnetic ordering temperature is estimated to be around 65(3)°K, which is lower by about 25°K than the values of FeOCl.

The intercalation of pyridine molecules resulted in a marked change not only in magnetic structure mentioned above, but also in the electrical conductivity, i.e., the electrical conductivity of FeOCl-pyridine complex ($\rho_{1c} \approx 2 \Omega\text{cm}$) being larger by a factor of 10^7 than that of FeOCl. Those changes may be explained by considering an interaction between the intercalated pyridine molecules and FeOCl layer.

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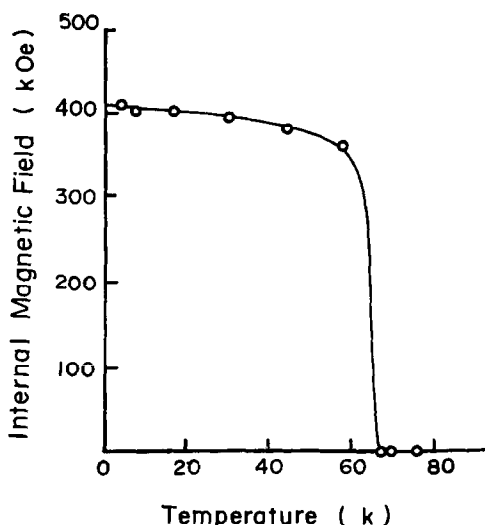


FIG. 4. Temperature dependence of the internal magnetic field of FeOCl(pyridine)_{1/3}.