

Paramagnetic Resonance of Mn-Palmitate and Mn-Stearate at 16 mm and 8 mm Wave-Lengths¹⁾

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Abstract

Mn-palmitate and Mn-stearate in powdered form have been investigated at room temperature by the method of microwave paramagnetic resonance absorption with 16 mm and 8 mm waves. The line-widths observed are about 400~550 oer. and the g -values are 2.00. From the intensity and the g -values, it may be concluded that a considerable portion of Mn atoms in our samples is Mn^{++} (in S -state). The absorption of Fe-stearate powder have been also observed. Its line-width is about 1500 oer. and its g -value is about 2.00.

Introduction

After Zavoisky's experiment in 1946⁽¹⁾, many experiments in microwave paramagnetic resonance absorption were performed in order to study the nature of paramagnetic ions in solid.

They can be classified into two groups: (a) the observations of the fine and hyperfine structure of an individual ion in magnetically diluted crystals⁽²⁾⁽³⁾, which make clear the magnetic behaviour of the electron spin of that ion under the influences of crystalline field, and (b) the studies of the shape of absorption curves in concentrated crystals⁽⁴⁾⁽⁵⁾⁽⁶⁾ from which we can deduce knowledges of the interaction of the ion with its surroundings.

As for organic compounds there have been several measurements in this region⁽⁷⁾⁽⁸⁾. In this article we shall report our results on the absorption of Mn^{++} in Mn-palmitate and in Mn-stearate and also of Fe^{+++} in Fe-stearate. These samples are made of the same material as the catalizer employed usually for the synthesis of oil.

Theory

Paramagnetic ions placed in a static magnetic field H absorb the microwave of frequency ν under the condition of

$$h\nu = g\beta H, \quad (1)$$

where h is the Planck constant, β the Bohr magneton and g the

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spectroscopic splitting factor.

The line-width of a peak in the case of non-diluted crystals is caused by the several reasons: (1) Dipole-dipole interaction of the ion absorbing the wave with other ions having magnetic moments, (2) Spin-lattice interaction, (3) Unresolved fine and hyperfine structures and (4) The averaging effect due to the anisotropic g -values of single crystal, in the case of powder.

Concerning the width of dipole-dipole origin, the "moment method" was developed by Van Vleck⁽⁹⁾. By his theory, the frequency width for the sample of powdered form is

$$\Delta\nu_{1/2} = 2.35 g^2 \beta^2 h^{-1} \left[\frac{3}{8} S(S+1) \sum r_{jk}^{-6} \right]^{1/2}, \quad (2)$$

where S is the total spin quantum number of an individual atom and r_{jk} is the distance from atom j to atom k . In case where the atomic configurations are not yet given, we use the "mean distance" a , assuming the cubic lattice, instead of r_{jk} , as a rough approximation. On the other hand, there is a relation

$$\frac{1}{a^3} = \frac{L\rho}{M}, \quad (3)$$

where L is the Avogadro number, ρ the density and M the molecular weight of the sample per one paramagnetic ion. Then Eq. (2) is transformed into

$$\Delta H = 5.74 \times 10^4 \sqrt{S(S+1)} \frac{\rho}{M}, \quad (4)$$

where ΔH is the half-value width in oer.

In our cases, both of Mn^{++} and Fe^{+++} are in 6S states and so we may put S to be equal to $\frac{5}{2}$. Then

$$\Delta H = 1.70 \times 10^5 \frac{\rho}{M}. \quad (5)$$

Experimental apparatus

The block diagram of our apparatus is shown in Fig. 1. K is a 2K25 klystron oscillator driven by a stabilized eliminator. M is harmonic multiplier using silicon crystal wafer and tungsten wire. For this experiment either of the power of the 2nd ($\lambda=16.55\text{mm}$) or of the 4th harmonics ($\lambda=7.82\text{mm}$) is sufficient but the stability of the latter is not adequate for the samples of weak and large width absorption. A is the attenuator used in order to secure correct line shapes. C is a rectangular cavity resonator operated in H_{102} mode and placed between the poles P of an electromagnet. The sample is mounted on the one of plungers and the cavity is tuned by the other. The loaded Q of 16 mm cavity with sample is the order of 3300 and that of 8 mm cavity is the order

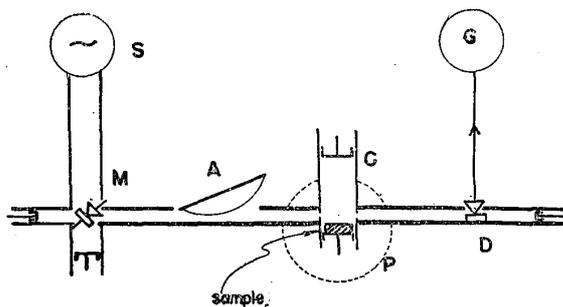


Fig. 1. Block diagram of the apparatus.

The strength of static magnetic field is determined by the fluxmeter calibrated by proton resonance. The g -values are obtained by comparing with the resonance peaks of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ powder or of α -diphenyl β -picryl hydrazyl.

Results and discussions

The results obtained are shown in Table 1 and a typical curve in Fig. 2. The absorption intensity of Mn-palmitate and Mn-stearate is fairly strong and of the order of one tenth of that of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$. The g -values of them are almost about 2.00. By these two reasons, we may infer that a considerable portion of Mn atoms in our samples are contained in the form of Mn^{++} (S -state).

The dipolar half-widths calculated by Eq. (5) are also given in Table 1, in which we have assumed that all the molecules of Mn-palmitate are $(\text{C}_{15}\text{H}_{31}\text{COO})_2\text{Mn}$ and those of Mn-stearate are $(\text{C}_{17}\text{H}_{35}\text{COO})_2\text{Mn}$.

A part of departure between the observed and the calculated widths must be due to the remaining origins of width, (2) and (3).

On the other hand, the experiments by Kumagai et al.⁽¹⁰⁾ show that, for Mn^{++} salts having large mean distances a , e.g. more than 6\AA as for $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ and diluted Mn Tutton salts, observed half-widths agree with those calculated by Eq. (5), and only for salts which have small a , the widths obtained are all smaller than those calculated. In our palmitate and stearate the values of a obtained from Eq. (3) are about 11\AA . Further, there are some reasons to suppose that our salt

of 200. D is a crystal detector and its rectified current is read by the galvanometer G . The magnitude of magnetic absorption A_m is expressed by

$$A_m \propto \left(\sqrt{\frac{\theta_0}{\theta}} - 1 \right), \quad (6)$$

where θ_0 is the galvanometer deflection at zero magnetic field and θ is that with field.

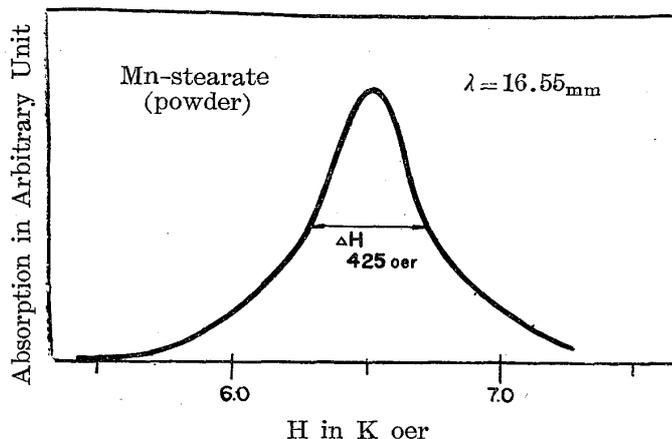


Fig. 2. Typical absorption curve of Mn-stearate.

of carboxylic acid may not be completely substituted to Mn salt from Na salt. By this reason, a greater value of a than that estimated by Eq. (3), and thence a smaller value of width than that determined by Eq. (5) should be used. But the observed widths are larger than that given by Eq. (5), as shown in Table 1.

One reason for this departure perhaps may be caused by the molecular shape of these salts. In solid state, the long chain type molecules may be in parallel with each other as shown in Fig. 3, so

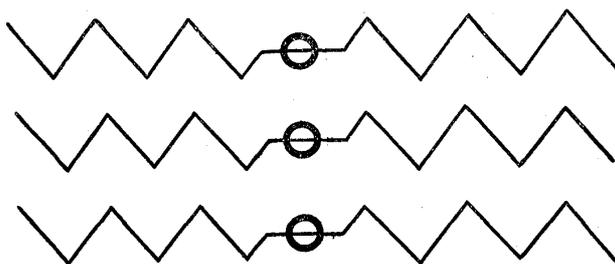


Fig. 3. Schematic view of shape molecules in solid state.

that the effective mean distances a_e are smaller than a used in the calculation of Table 1 with the assumption of cubic configuration.

The similar results for Fe^{+++} in Fe-stearate are shown in Table 2. Since the absorption intensity is weaker than that of Mn salts, the experimental errors of the results become larger. By the same reason as in the case of Mn, in our sample, several tenths of Fe atoms may be Fe^{+++} in the form of $(\text{C}_{17}\text{H}_{35}\text{COO})_3\text{Fe}$. The departure between the observed and the calculated values is more remarkable.

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Table 1. Observed half-value width in oer. and g-values compared with calculated ones in Mn salts.

Samples used	Mn-palmitate		Mn-stearate	
	ΔH in oer.	g-value	ΔH in oer.	g-value
Observed values in 16.55 mm	550 ± 50	2.00	410 ± 10	2.00
Observed values in 7.82 mm	410 ± 60	2.00	380 ± 40	2.00
Calculated values by Eq. (5)	260	—	260	—

Table 2. Observed half-width and g-value compared with calculated one in Fe salts.

Samples used	Fe-stearate	
	H in oer.	g-value
Observed values in 16.55 mm	1500 ± 100	2.01 ± 0.01
Calculated value by Eq. (5)	175	—

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