

Determination of the Magnetic Moment of α -Fe₂O₃ of the Parasitic Ferromagnetism by the Proton Relaxation in Water

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A theoretical expression for determining the effective magnetic moment of hematite(α -Fe₂O₃) particle of the parasitic ferromagnetism by the proton relaxation in water is derived. In deriving the expression it is found that the mathematical procedures are exactly the same as those applied for aqueous solutions containing free paramagnetic ions, except that the distance between the proton spin of water molecule and the corresponding electronic spin of the particle must be considered to be a radius vector rather than a relative distance. And it is also found that the average effective magnetic moment of the particle calculated by the expression is in good agreement with the experimental value determined by Hirai.

I. Introduction

It is known that hematite(α -Fe₂O₃) is antiferromagnet and it is accompanied by a weak ferromagnetism above the transition temperature of -15 °C, which is called "parasitic ferromagnetism"¹⁻³. In this work an attempt is made to derive a theoretical expression for determining the average magnetic moment of the hematite crystalline particle in powder form by using the well-known relaxation theories applied to aqueous solutions with paramagnetic ions⁴. To derive the expression the following assumptions are made for simplicity :

A. A solid surface adsorption effect is disregarded.

B. Each hematite particle is regarded as a sphere as the water molecule.

C. The proton spin of the water molecule and the "corresponding unpaired electronic spin*" of the hematite in powder form are designated by I and S , respectively. The interaction between I and S is a dipole-dipole interaction of unlike spins.

D. The hematite particles are uniformly suspended in water for effective contributions to the proton relaxation designated by $(1/T_1)_h$. Except for the particles suspended in water, the situation is considered to be similar to the one of the aqueous solutions with paramagnetic ions.

E. The distance designated by r between the unlike spins is a radius vector rather than a relative distance, since the water molecules diffuse relative to the fixed hematite particles which are suspended in water.

II. Effective Magnetic Moment

By virtue of the assumptions A to D, the mathematical procedures are exactly the same as those⁴ treated for aqueous solutions containing paramagnetic ions. Here the relaxation, $(1/T_1)_h$, is just given by⁴

$$\left(\frac{1}{T_1}\right)_h = \gamma_1^2 \mu_{\text{eff}}^2 \left[\frac{1}{12} J^{(0)} + \frac{3}{2} J^{(1)} + \frac{3}{4} J^{(2)} \right] \quad (1)$$

where γ_1 is the gyromagnetic ratio of the proton, μ_{eff} is the effective magnetic moment of the corresponding electronic spin, and the J 's are the Fourier spectral intensities. It is noted that the

*) Since a single hematite crystalline particle can not simply be regarded as a single transition metal ion with unpaired electronic spins, an electronic spin corresponding to an effective magnetic moment of the particle is called the corresponding unpaired electronic spin for convenience.

superscripts of the intensities correspond to the random functions of the positions of I relative to S fixed.

By virtue of the assumption E, the water molecules are in the random Brownian motion relative to the fixed hematite particles. Hence the solution of the diffusion equation⁴, $\Psi(\vec{r}, \vec{r}_0, t) = (4\pi Dt)^{-3/2} \exp[-(\vec{r} - \vec{r}_0)^2/4Dt]$, becomes the probability that the distance connecting the two axes of the unlike spins of I and S has certain displacements at given time, t , relative to the fixed axis of the corresponding electronic spin, which is the only difference between the free ions and the suspended particles. For this the Fourier spectral intensities in Eq.[1] obtained by exactly following the mathematical procedures⁴ are given by

$$\begin{aligned} J^{(0)} &= 384 \pi N / 225 \epsilon D_w \\ J^{(1)} &= 64 \pi N / 225 \epsilon D_w \\ J^{(2)} &= 256 \pi N / 225 \epsilon D_w \end{aligned} \quad (2)$$

where N is the number of the electronic spins per cubic centimeter, ϵ the minimum distant of approach between the molecule and the single particle and D_w the translational diffusion coefficient of the water which is given by $kT/6\pi a\eta$. Here k is the Boltzmann constant, T the absolute temperature, a the radius of the molecule and η the viscosity of water.

Substituting the results in Eq.[2] into Eq.[1], $(1/T_1)_h$ becomes

$$(1/T_1)_h = 64\pi \gamma_1^2 \mu_{\text{eff}}^2 N / 45 \epsilon D_w \quad (3)$$

Now, as shown before⁵, the total contribution to the proton relaxation designated by $1/T_1$ is given by

$$\left(\frac{1}{T_1}\right) = \left(\frac{1}{T_1}\right)_w + \left(\frac{1}{T_1}\right)_h \quad (4)$$

from which μ_{eff} is obtained as

$$\mu_{\text{eff}} = \left[15 \epsilon k T \left\{ \left(\frac{1}{T_1}\right) - \left(\frac{1}{T_1}\right)_w \right\} / 128 \pi^2 \gamma_1^2 a \eta N \right]^{1/2} \quad (5)$$

Here $(1/T_1)_w$ is the proton relaxation in water in the absence of the particles. The experimental value⁶ of the relaxation in pure water, $(1/T_1)_w$, is given by 0.27 sec^{-1} .

III. Results and Discussion

To determine the effective magnetic moment of $(1/T_1)_h$, N must first of all be calculated as the following ways: Since the edge length of the rhombohedron unit cell of the hematite^{1,7} is 5.42 \AA and the angle of the unit cell is $55^\circ 17'$, the volume of the cell designated by V_0 is roughly given by $V_0 = 1.31 \times 10^{-22} \text{ cm}^3$. By virtue of the assumption B, the volume of the single hematite particle in powder form designated by V_h is equal to $V_h = 4\pi d^3/3$. Here d is the average radius of the particle. Since there are two corresponding Fe ions in the unit cell, the number of the corresponding electronic spins in the single particle with the radius designated by N_s is approximately given by $N_s = 2(V_h/V_0)$. If N_h is the number of the particles with the radius, d , in powder form per cubic centimeter, then N in Eq.[5] is given by $N = N_h N_s$.

The following experimental results⁸ are used only for the purpose of examining whether Eq.[5] is valid: For given $d = 10$ microns, $1/T_1 = 0.18 \text{ sec}^{-1}$ for $N_h = 1.82 \times 10^5 \text{ #'s/c.c.}$, $1/T_1 = 0.14 \text{ sec}^{-1}$ for $N_h = 2.74 \times 10^5 \text{ #'s/c.c.}$, $1/T_1 = 0.15 \text{ sec}^{-1}$ for $N_h = 3.65 \times 10^5 \text{ #'s/c.c.}$ and $1/T_1 = 0.14 \text{ sec}^{-1}$ for $N_h = 4.56 \times 10^5 \text{ #'s/c.c.}$

Table I shows the effective magnetic moments

Table I. For respective experimental values of $1/T_1$, calculated N and μ_{eff} .

$N(\times 10^{18} \text{ #'s/c.c.})$	$1/T_1(\text{sec}^{-1})$	μ_{eff} (in Bohr magneton)
11.63	0.71	0.18
17.51	0.71	0.14
23.32	0.83	0.15
29.14	0.91	0.14

calculated along with the above given values.

From Table I, the average effective magnetic moment in Bohr magneton is given by 0.15. Here it must be noted that the minimum distance of approach, ϵ , is taken to be 2.34×10^{-8} cm, for the radius of the molecule is 1.74×10^{-8} cm and the radius of the corresponding Fe ions 0.60×10^{-8} cm.

Since the saturation magnetization of α -Fe₂O₃ obtained by Hirai³ is 2.1 emu/c.c. equivalent to 0.14 in Bohr magneton, the above calculated average effective magnetic moment, 0.15 in Bohr magneton, is in very good agreement with each other. For this it is concluded that Eq.[5] is valid.

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물의 양성자완화에 의한 기생 강자성 α -Fe₂O₃의 자기능률 결정

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물의 양성자완화에 의하여 기생 강자성 α -Fe₂O₃의 유효 자기능률 결정을 위한 이론식을 유도하였다. 그 이론식을 유도함에 있어서 그 결정입자의 대응전자스핀과 물분자의 양성자 스핀사이의 거리가 상대적 거리보다 오히려 동경 벡터로 고려되어야 한다는 사실을 제외하고서 자유 상자성 이온들을 함유하고 있는 수용액에 적용된 수학적 과정과 정확히 동일하다는 것을 알았다. 또한 유도된 이론식에 의하여 계산된 결정입자의 유효자기능률이 Hirai에 의하여 결정된 실험치 잘 일치함을 알았다.