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The Particle Size Dependence of the Néel Temperature of α-FeOOH Fine Particles

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The particle size dependence of the Néel temperature of α-FeOOH was studied experimentally. The Néel temperature decreased with decreasing particle size and the α-FeOOH of 2000Å in particle size showed the Néel temperature which was about 9% lower than the of the bulk specimen.

I. INTRODUCTION

In recent years α-FeOOH has been the subject of the Mössbauer and other magnetic studies. There are, however, great discrepancies between the experimental results. The Néel temperature of this compound, determined from the magnetic susceptibility or from the temperature dependence of the internal field, spreads over the wide temperature range. Szytuza *et al.* reported 330°K[1] as the Néel temperature, whereas 440°K was given by Oosterhout[2]. The previously reported values of the Néel temperature were summarized in Table 1.[3,4] It was suggested by some authors that the discrepancy may be due to the defect structure in the samples. However, clear explanation has not been given yet. In this work the dependence of the Néel temperature on the particle size of α-FeOOH was studied with the purpose of elucidating this problem.

Table 1. Reported Néel Temperature of α-FeOOH.

Reference	Néel Temperature	Method
1)	330°K	Mag. Sus.
1)	320∼370°K	Mag. Sus.
2)	440°K	Mag. Sus.
3)	393°K	Möss. effect
4)	400°K	Möss. effect

II. EXPERIMENTAL

1. Sample Preparation

Four samples of α-FeOOH were prepared. One sample (A–1) was made by the oxidation of the suspension of Fe metal with the air. Detailed description of reaction method was given in the precedented paper.[5] The other three samples (A–2, A–3 and A–4) were prepared in the following way.

200g of $Fe(NO_3)_3 \cdot 9H_2O$ was dissolved in distilled water, then 89 g of NaOH was added to the solution. Resultant brown precipitates, which were amorphous in the x-ray analysis, were aged for 24 hr at room temperature. After that the hydrolysis reaction was carried out on these precipitates at 80°C, 95°C and 130°C respectively.

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With the proceeding of the reaction the amorphous precipitates were gradually converted to yellow precipitates of α-FeOOH. The α-FeOOH precipitates thus obtained were filterd, washed with distilled water and dried at 80°C. X-ray and near-infrared analysis affirmed that these precipitates consisted of α-FeOOH only. No other element than Fe, H and O was detected by chemical analysis.

2. Measurement

The Néel temperature T_N of α-FeOOH was determined by the temperature dependence of the internal field Hi of the Mössbauer spectrum. The magnetic susceptibility measurement was also used as a subsidiary method.
Particle size was determined by electron micrography and gas adsorption method (B.E.T. method).

III. RESULT AND DISCUSSION

In Fig. 1 the temperature dependence of Hi observed in samples of A–2 and A–4 are given. In Fig. 2 some of the spectra of these samples observed at different temperatures 296°K, 340°K and 355°K are shown. Both samples exhibit ordinary temperature dependence of Hi, but nevertheless the observed absolute values of Hi are different especially in high temperature range. The temperatures, at which the collapse of Hi occurs, are determined to be 395°K and 365°K by the extrapolation, respectively. The temperature dependence of Hi of the samples of A–1 and A–3 shows the same tendency and the collapse of Hi occurs at 400°K and 386°K. The temperature dependences of the magnetization curves of the sample A–1, A–2, A–3 and A–4 are given in Fig. 3. In these curves two characteristic behaviors are observed. One is the magnetic cooling effect and the other is the appearence of the broad maximum at the different temperatures. For example, sample A–4 shows the peak at 365°K and below this temperature magnetic cooling effect is observed. The temperature where the peak was observed coincided with the temperatures at which collapse of Hi were observed.

In Fig. 4 an electronmicrograph of sample A–2 is given. From this photograph it is seen that α-FeOOH particle have rectangular shape. Regardless of the particle size, the ratio of three edges of the rectangle that are the longest, middle and the shortest is always 10;1;0.3 approximately. In other words, α-FeOOH particles are isomorphous. Hereafter we represent the particle size with the length of the longest edge. The average particle size are summarized in the second column of the Table 2. The particle size is the largest (2μ) for sample A–1 and it decreases with increase of the sample number. The smallest particle size (A–4) is 2000Å.

In disscussing it must be proved first that the temperature determined by the extrapolation, where the collapse of Hi occurs, is true T_N. In fine particles there exists possibility that thermal fluctuation of the electron spins gives deceptive T_N. This phenomenon, usually observed in the magnetic susceptibility measurement is called superparamagnetism. In the Mössbauer spectrum thermal fluctuation effect was calculated theoretically by Blume and Tjon[6] as a function of the relaxation time. Otherwise the equation for the size dependence of relaxation time was given by Néel[7]. These two theories indicate that true T_N is obtained by the extrapolation of the temperature vs. Hi curve of the Mössbauer spectrum even if the thermal fluctuation effect exists. This is shown in Fig. 5 shematically. In this figure solid and dotted

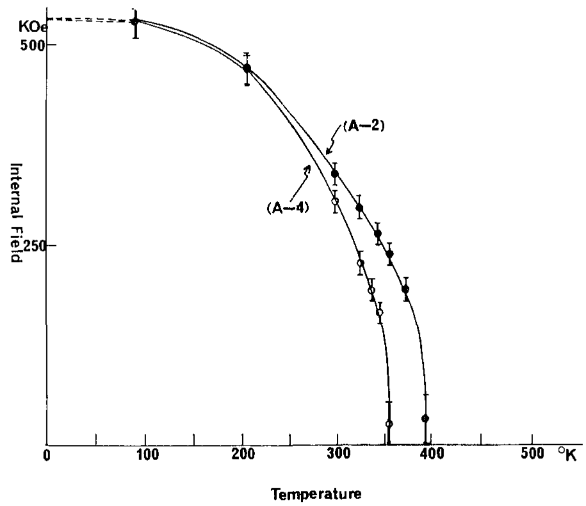

Fig. 1. The temperature dependence of the internal field of Mössbauer spectra of sample A-2 and A-4.

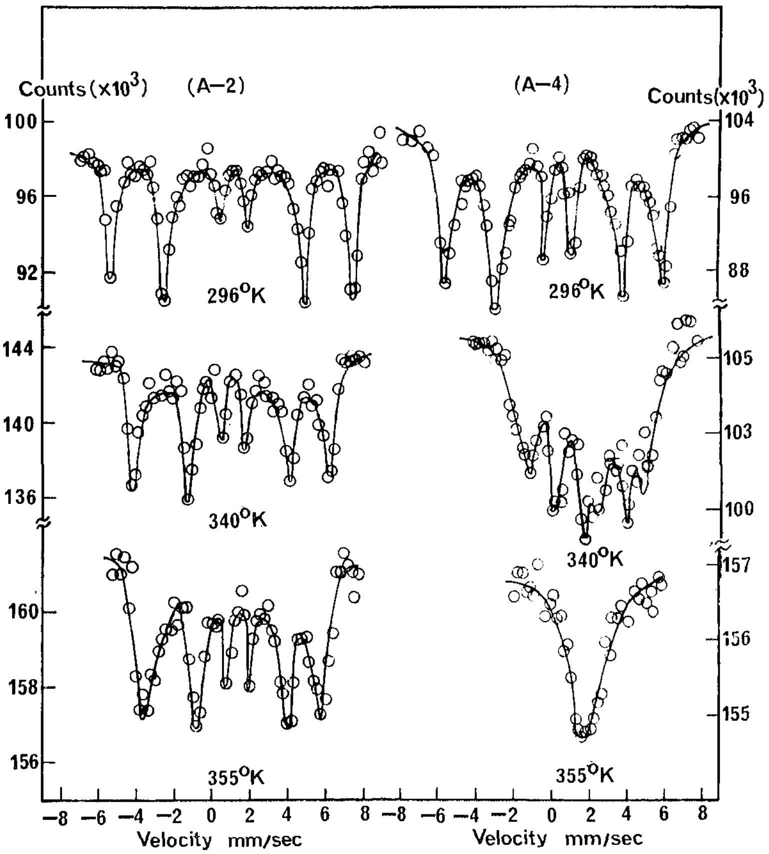

Fig. 2. The observed spectra of sample A-2 and A-4 at 296°K, 340°K and 355°K, respectively.

lines exibit the expected temperature dependence of Hi under the influence of the thermal fluctuation effect in the case of different T_N. From above disscusions it is apparent that the temperature determined by the extrapolation gives true T_N. The

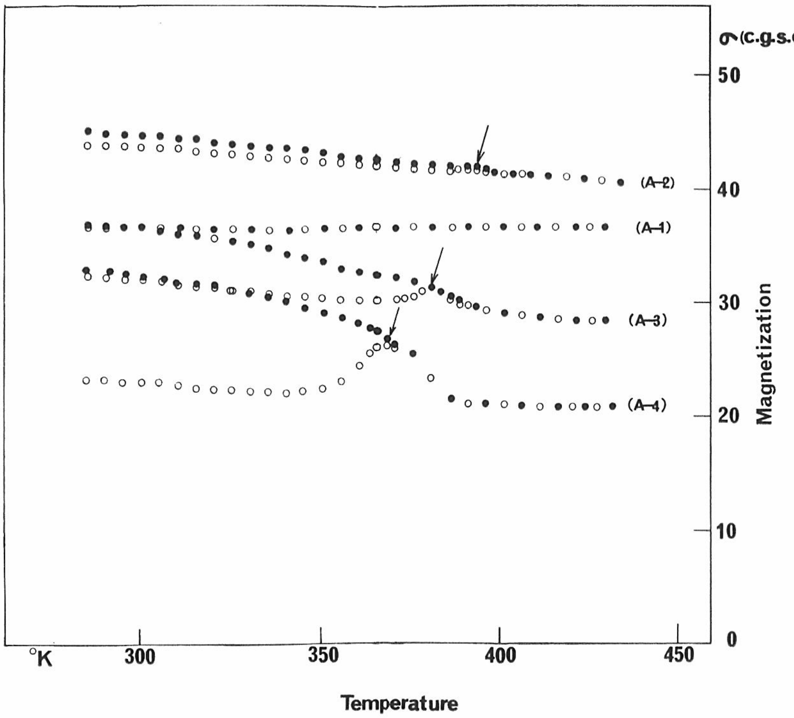

Fig. 3. The temperature dependence of the magnetization curves of sample A-1, A-2, A-3 and A-4, respectively. The arrow shows the Néel temperature of each sample.

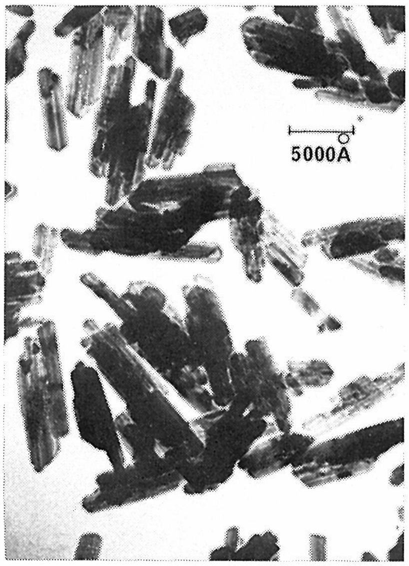

Fig. 4. Electronmicrograph of sample A-2.

data summarized in Table 2 show that in these samples T_N decreases with decreasing particle size. In Fig. 6 particle size dependence of T_N is given graphically.

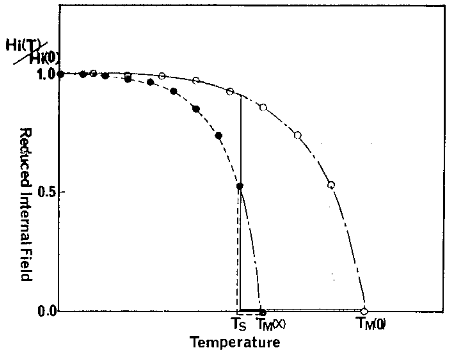

Fig. 5. The expected temperature dependence of the internal field under the influence of the thermal fluctuation effect in the case of different Néel temperatures.

Table 2. Observed Particle Size and Néel Temperature.

Sample	Particle Size	Néel Temperature
A-1	$<1\mu$	400°K
A-2	6000 Å	395°K
A-3	4000 A	387°K
A-4	2000 A	365°K

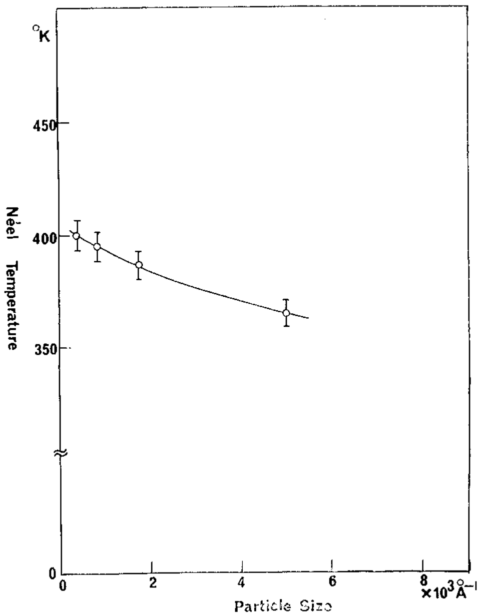

Fig. 6. The observed particle size dependence of the Néel temperature.

It is concluded from the present experiment that such factors as the contamination by foreign ions and the change of the lattice parameter are discarded and the decrease of T_N is brought out by the decrease of the particle size. Concerning size dependence of the magnetic ordering temperature only few papers were published both in the theoretical and experimental fields. Dresselhaus obtained the exact solution of T_C in the case of Heisenberg ferromagnet of 8 spins in cubic lattice. In this case T_C is about a half of the infinite system of the same lattice. In the case of α-FeOOH the number of the magnetic ions is about 10^4 and so it is impossible to get the exact solution of T_C. In stead of the exact solution it may be possible to explain this decrease of T_N based on the model adopted in the explanation of the decrease of T_N in dilute ferrites.[9~11)]

This model assumed that T_N depends on the average number of the magnetic bonds per magnetic ion and the decrease of T_N begins with the substitution of the magnetic ions with nonmagnetic ions. In the case of α-FeOOH vacancy and the surface take the place of the nonmagnetic ions (It seems natural that the density of the vacancy increases with decreasing particle size from the magnetic data and the surface also increases with decreasing particle size). As an example, in α-FeOOH of 2000Å in size and of 5% vacancy density, T_N is expected to show about 10% lower value than that of the bulk specimen. Further quantitative discussion is impossible, however, because of the difficulties in estimating the amount of the vacancy in the sample.

IV. CONCLUSION

The present study has shown that T_N of α-FeOOH exibites the particle size dependence and the size dependence is one of the origins of wide divergence of T_N reported for this compound.

It seems probable that the size dependence of T_N is as a result of the increasing vacancy and the surface with decreasing particle size and the same effect is expected to occur in the all kinds of magnetic fine paticles.

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