JOURNAL OF MATERIALS SCIENCE 31 (1996) 519–535

Angular variation of coercivity of interacting fine acicular skeleton particles

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For fine, acicular skeleton particles of α-Fe prepared from α-FeOOH, the effect of interparticle interaction on the angular variation of H_c was numerically investigated using a direct expansion scheme of the "chain-of-spheres" fanning model to an interacting chain system forming an orthorhombic type of regular space lattice. The model theory reveals that only magnetostatic lateral interchain interaction can affect the angular variation of H_c. The results have been used to explain the experimentally observed effects of particle morphology and packing fraction on the angular variation of H_c in systems made from fine acicular particles prepared for audio/video magnetic recording media. It is suggested that a local aggregate of the so-called "multiple" type, is unavoidably generated in the system.

1. Introduction

Fine acicular particles of α–iron (α-Fe) prepared for high-density audio and/or video recording media, are industrially synthesized from nearly the same dimensional and chemically modified particles of goethite (α-FeOOH) via dehydration, calcination and reduction under an inert gas and/or a hydrogen atmosphere. The particle of α-Fe thus obtained consists of crystal grains and is of the *skeleton particle* type, which is a well-defined technical term in the field of electron microscopy.

In previous papers [1–5], we studied the relationship between the skeleton-particle morphology of α-Fe and the magnetic properties. In particular, we investigated numerically [4] the particle–particle interaction effect on packing-fraction (ρv) dependence of coercivity, (H_c), under a direct expansion scheme of the "chain-of-spheres" fanning model (CSFM) to an interacting chain system forming an orthorhombic type of regular space lattice, where the CSFM developed originally by Jacobs and Bean [6] has been modified by the author to reflect correctly the experimentally observed skeleton-particle morphology. The roles of the morphology, interparticle interaction and geometrical configuration of the particle location were quantitatively investigated and it was shown that the model theory can explain the experimentally observed effects of the particle morphology and the packing on H_c for the realistic fine, acicular skeleton particles of α-Fe, including many published data about γ-Fe_2O_3 or α-Fe.

As a second result of our tests to investigate the effects of interactions among the skeleton particles on the reversal of magnetization, the effect of the alignment angle, ψ (defined as the angle between the major axis of the acicular particle and the direction of an external magnetic field) on H_c is also reported in the present paper [7].

2. Experimental procedure and theoretical treatment

2.1. Procedure

Because the problem of the angular variation of H_c (AVH_c) is very important in read/write characteristics of magnetic recording media, many experimental evaluations have been carried out (for example [8–13]).

(a) For coating material made from fine, acicular particles of γ-Fe_2O_3 or α-Fe, it has been commonly found that H_c increases monotonically with increasing ψ up to about 55–60°, above which H_c decreases rapidly. Furthermore, in the case of the particles of α-Fe, we found that AVH_c depends strongly on the particle morphology [1].

(b) It has been experimentally observed that the peak value in the AVH_c decreases gradually with increasing packing, if the value of H_c at $\psi = 0°$ is normalized to unity.

The behaviour for the lower range of ψ in (a) can be attributed to an incoherent mode of the reversal of magnetization which has first been found by Jacobs and Bean [6], while the behaviour for higher ψ in (a) was semi-quantitatively and theoretically explained by us [2]. The behaviour in (b), which will be caused by the interaction effect, must be explained if the theoretical treatment of the angular variation problem of H_c is properly developed. As far as the author knows, this is one of the unsolved problems about H_c in systems of the many interacting particles.

2.2. Theoretical treatment

As in [2], we assume that the apparent morphology of the fine, acicular skeleton particle can be geometrically represented by a modified "chain-of-spheres" that are characterized by a number of unit spheres, n, and by a contact angle, α (deg), between two adjacent

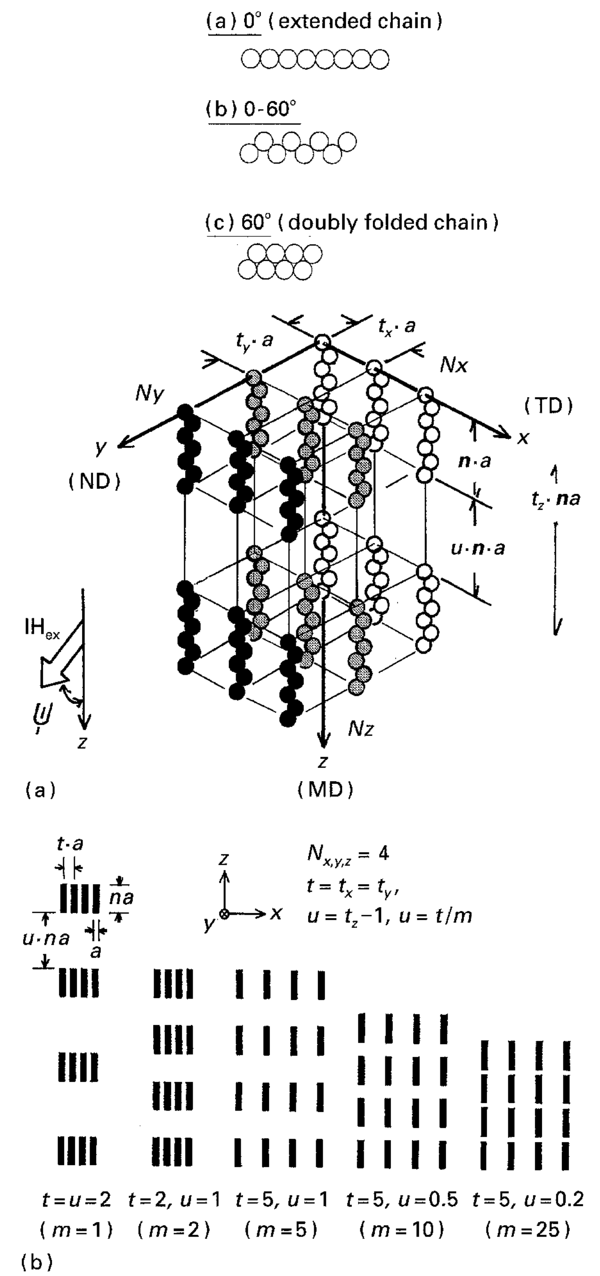

Figure 1 SJBC and space co-ordination of three-dimensional interacting chains. (a) Definition of contact angle, α, of SJBC and space lattice characterized by its size, (Nx, Ny, Nz), and lattice constants, (t_x, t_y, t_z). (b) Demonstrative illustration of chain-location by lattice constants, t and u or convenient parameter m: the SJBCs configuration can be specified by (t, u) or (t, m) or $(m, \rho v)$ for a finite space lattice of (Nx, Ny, Nz). m was introduced to characterize a geometrical configuration of the SJBC Location, as illustrated by this figure. (Courtesy of Elsevier Science Publishers B.V., Fig. 2(b) and Fig. 3 of [4]).

unit spheres. (This type of chain is hereafter referred to as "snaked" Jacobs–Bean's chain-of-spheres or *SJBC*, because such a morphologically modified chain "snakes" locally). As in [4], we consider an assembly composed of fine, acicular skeleton particles, whose morphology can be represented by the above SJBCs and whose magnetizations can be induced via the "CSFM". Here, we hypothesize that it is possible to represent the particle assembly by a "finite" three-dimensional orthorhombic regular space lattice that can be characterized by its size, Nx, Ny and Nz, its volumetric packing fraction of the chains, ρv, and a parameter reflecting the geometrical configuration of the SJBC's location, m, see Fig. 1.

The AVH_c for the assembly with given ρv and m is computed for various types of SJBC. The procedure for the numerical calculations is the same as that described elsewhere [4], except that the lattice size was fixed to be $(Nx, Ny, Nz) = (10, 10, 10)$ in order to save CPU time of the computer, if a three-dimensional lattice is considered.

3. Calculated results

3.1. Regular SJBCs

First, in order to estimate the effect of the *axial* and *lateral* interactions (AI and LI) on the AVH_c, two types of a one-dimensional lattice composed of extended-type interacting SJBCs with $(n, \alpha) = (10, 0)$ were assumed: $(Nx, Ny, Nz) = (1, 1, 10)$ and $(10, 1, 1)$, respectively. Here, AI and LI indicate the interchain interaction along and across the chain axis, respectively [4]. Hereafter, the value of H_c calculated theoretically is taken in units of μ/a^3, where μ and a denote the magnetic dipole moment and the diameter of the unit spheres of SJBC, respectively.

Examples of the results are shown in Figs 2 and 3: Fig. 2 shows the AVH_c for the one-dimensional lattice with $(Nx, Ny, Nz) = (1, 1, 10)$ where ρv was assumed to be 0, 85% or 100%. It should be noted that the state with ρv of 0 or 100% corresponds effectively to a single isolated chain with $n = 10$ or 100, respectively. It can clearly be seen that the dependence of H_c on ψ is essentially the same. This can physically mean that the dependency of H_c on ψ is hardly affected by AI. On the other hand, as shown in Fig. 3, the AVH_c for the one-dimensional lattice with $(Nx, Ny, Nz) = (10, 1, 1)$ (that is one-dimensional *raft* type lattice) is strongly influenced by the LI. In the cases of the higher packing states, H_c does not increase with increasing ψ even below 50°. This effect of the LI on the angle-dependence of H_c at the high packing state must be remembered if the AVH_c of the three-dimensional lattice is quantitatively analysed.

Next, the AVH_c of the finite three-dimensional lattice composed of the extended type of the interacting SJBCs with $(n, \alpha) = (4, 0)$ or $(10, 0)$ were estimated for several values of ρv and m. Typical results are shown in Fig. 4a and b. Adding the results obtained for the interacting SJBCs with $(n, \alpha) = (4, 0)$, it is commonly observed that H_c increases monotonically and then decreases rapidly with increasing ψ.

(a) The increasing behaviour of H_c with ψ can be attributed to an incoherent mode of the CSFM, while the decreasing behaviour is attributed to a coherent mode.

(b) The transition angle from the incoherent to the coherent mode depends on the chain length, the packing fraction and the chain location mode: generally, the larger AI, corresponding to larger n and also larger m, and the weaker the interaction, resulting from diluted packing states, provide the smaller value of the transition angle.

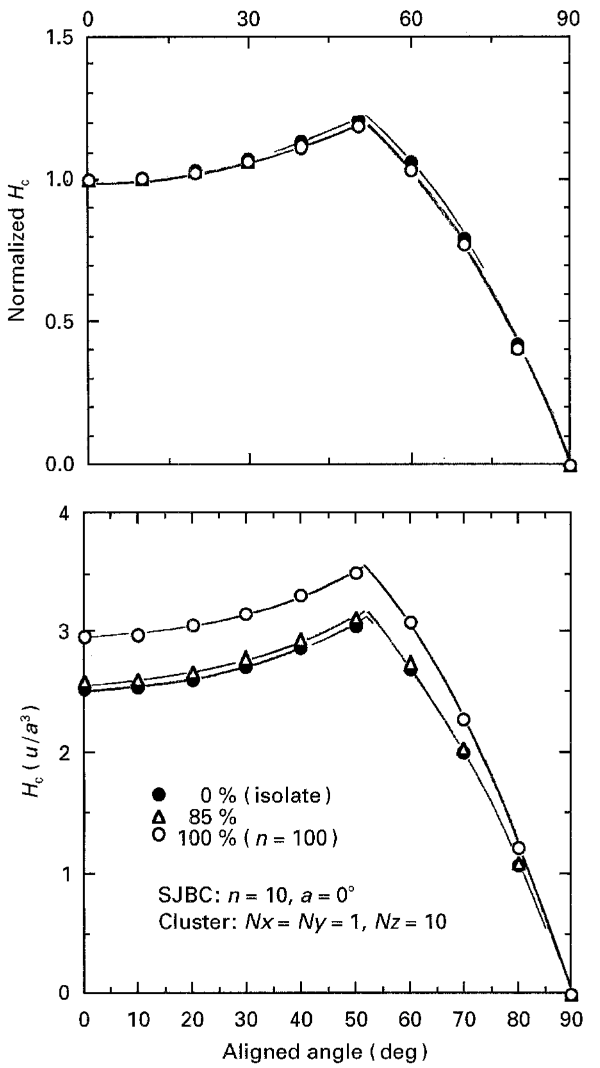

Figure 2 Effect of "axial interaction" on angular variation of H_c. Linearly arranged Jacobs–Bean's chains along their chain axes are taken into account. The percentages in the figure indicate the volumetric packing density of the chains.

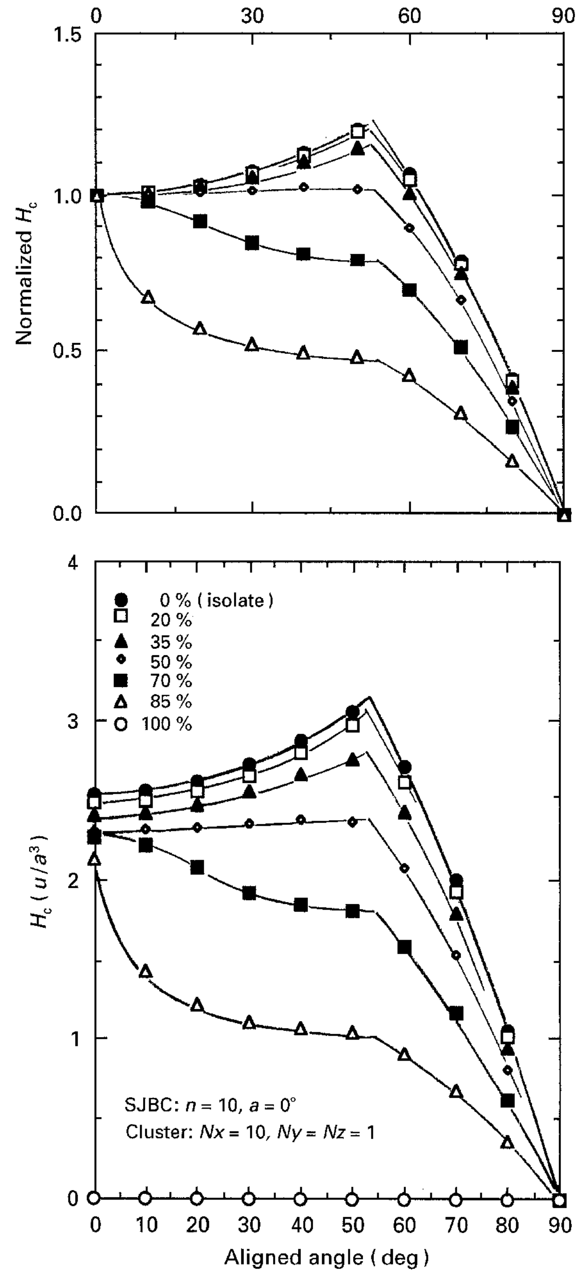

Figure 3 Effect of "lateral interaction" on angular variation of H_c. Laterally aranged Jacobs-Bean's chains forming just like a "raft" are taken into account. The percentages in the figure indicate volumetric packing density of the chains.

(c) If the value of H_c is normalized at $\psi = 0°$ to be unity, the larger AI results in a smoother angular variation of H_c.

3.2. Effect of realistic packing

In the coated material made from fine acicular skeleton particles of α-Fe, we have found that the geometrical location mode of the particles depends on the packing: the parameter, m, increases almost monotonically with increasing ρv (Fig. 11a of [4] and Fig. 28b of [5]). Therefore, the AVH_c of the assembly composed of SJBCs of $(n, \alpha) = (10, 0)$ with m of 5, 10, 30 and 40 were estimated at the packing of ρv of 5%, 10%, 30% and 40%, respectively.

The results obtained are partly shown in Fig. 5. In this case, although the value of H_c at $\psi = 0°$ decreases slightly, the angle dependence of H_c does not essentially change. This behaviour should be remembered if the experimental effect of the packing on the AVH_c observed for the coated material is quantitatively analysed.

3.3. Effect of particle morphology

To estimate the effect of the particle morphology on the AVH_c, the value of (n, α) of SJBC was changed to (24, 45) and (40, 60), where the former and latter SJBCs can represent a planar zig-zag chain (or the partially porous particle) and a type-D particle [4, 5], respectively. It may be noted that the aspect ratios of both the SJBCs are nearly 10, which is a typical value for the very fine acicular particles used for magnetic recording media.

The results obtained are shown in Fig. 6a and b. In these cases, the angle dependence of H_c is apparently quite different from that of SJBC with (n, α) of (10, 0). However, the effects of the chain packing and location mode are essentially the same as that found for SJBC with (n, α) of (10, 0).

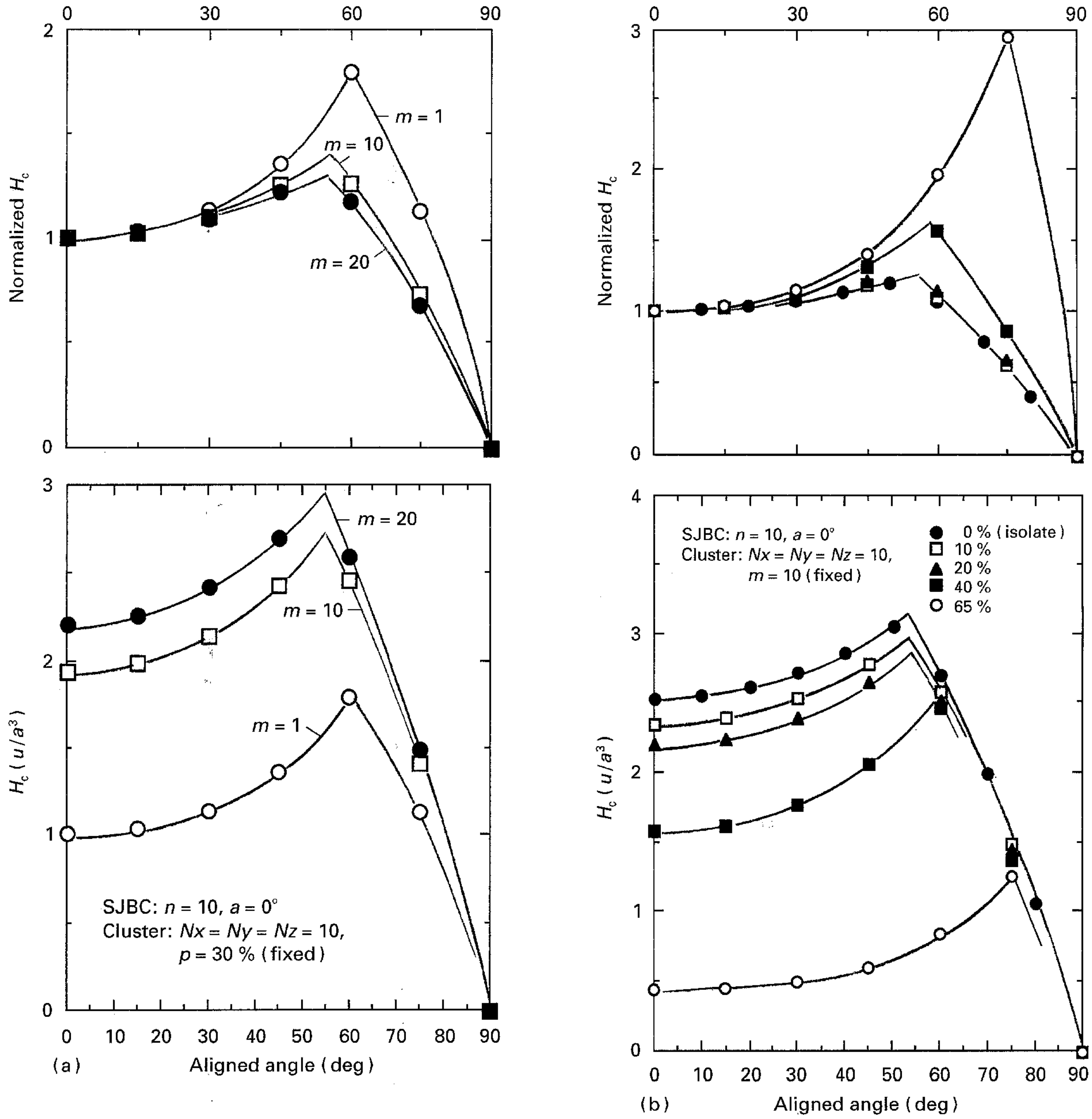

Figure 4 Angular variation of H_c of a finite three-dimensional lattice forming an orthorhombic type. (a) Effect of a chain location mode at fixed packing state. (b) Effect of a packing degree for a fixed chain location mode.

Next, the effect of the intraparticle pores on the AVH_c was investigated, where the pores were physically interpreted as defect sites caused by an intergrain misfit and mathematically represented by introducing dipole-less spheres into SJBC [3]. Here, without a loss of generality, SJBCs with (n, α) of (10, 0) having two defective sites (4th and 7th unit spheres), (24, 45) having four defective sites (5th, 10th, 15th and 20th unit spheres), and (40, 60) having ten defective sites (5th, 8th, 11th, 14th, 17th, 20th, 25th, 28th, 31st and 34th unit spheres) were taken into account [3]. Furthermore, it was assumed that a symmetric fanning mode of the magnetization reversal is available for the former two kinds of SJBCs and a modified symmetric fanning mode for the latter kind of SJBC [3]. A typical result is shown in Fig. 7, from which it can be seen that introducing the intraparticle pores leads to a steeper dependence of H_c on ψ.

From these results, it will be concluded that only the LI can affect significantly the dependence of H_c on ψ. Furthermore, as pointed-out by Cecchetti [14], it should be noted that a relatively strong LI provides an AVH_c apparently similar to that given by the completely coherent reversal of the magnetization of the ellipsoidal particle [15].

4. Application to experiments

Experimental data for the AVH_c for very fine, acicular particles useful for magnetic recording media observed by us and reported by many researchers, are quantitatively analysed in this section.

4.1. Iron particles and fundamental aspect to be hypothesized

A typical example of (b) described in the Section 2.1. is shown in Fig. 8 [7], where the experimental AVH_c observed in two nominally uniaxially oriented tape materials that were made from very fine, acicular

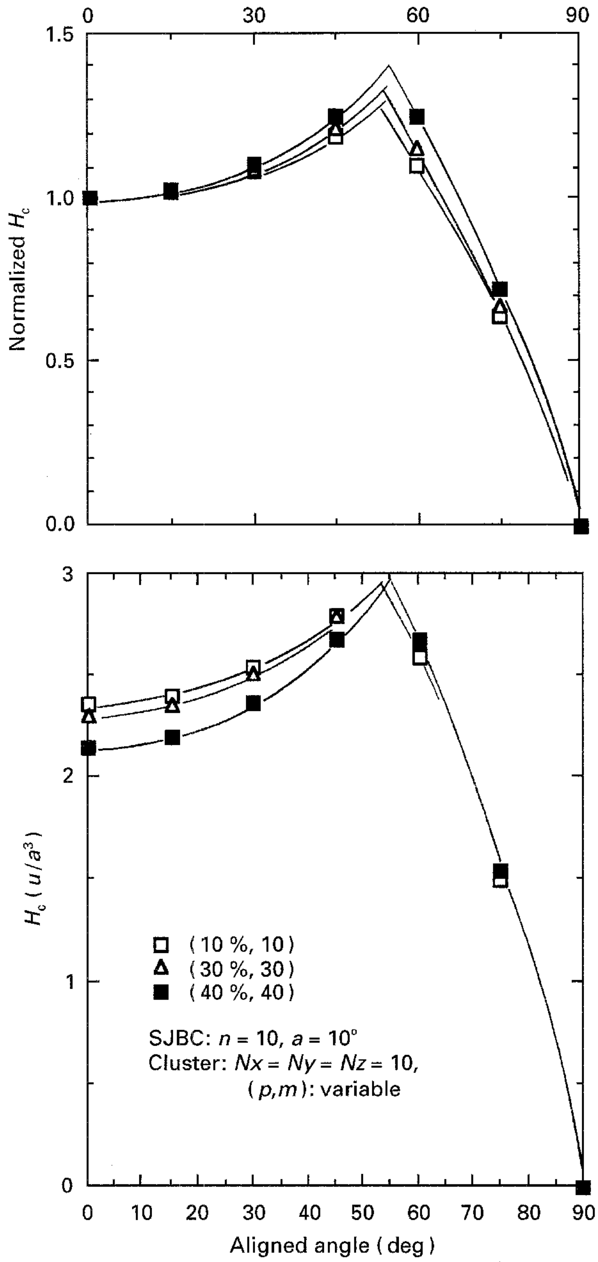

Figure 5 Angular variation of H_c of a finite three-dimensional lattice having a chain location mode changing with a packing degree.

particles of α-Fe with different packing, p, are provided in two ways: the experimental raw data and the normalized representation. The particles were industrially synthesized for use as audio recording media. The average crystal-grain size of the particles was about 20 nm, which was estimated by transmission electron microscopy (TEM). The average aspect ratio of the particles was about 10. Microscopic pores of about 7%–8% by volume, were found in the particles. This skeleton-particle morphology can be classified into "type-S" in terms of our definition of the very fine, acicular particle morphology [4]. As was already stated elsewhere [4], according to the method given by Grimwood *et al.* [16], p of the tape materials shown in Fig. 8 was controlled by using fine acicular particles of iron oxide (haematite) with approximately the same dimensions as the iron particles mentioned above.

In Fig. 8a, the experimentally measured raw data of the AVH_c are shown. Because the tape materials used here are nominally uniaxially oriented, H_c at $\psi = 90°$ (which reflects the reversal of the magnetization along the "perpendicular direction") has a non-zero value, which is a contribution from the unavoidable co-existence of a finite number of non-oriented, randomized particles. Although Jacobs and Luborsky [9] had proposed a method of calculating the contribution of the non-oriented components in such systems, the normalized AVH_c in Fig. 8b, however, is defined by $[H_c(\psi) - H_c(90)]/[H_c(0) - H_c(90)]$. This representation comes from a tentative assumption that the magnetic interaction between the oriented and not-oriented components of the particles can be negligible. See also Appendix A, from which the effect of the packing on the AVH_c of the perfectly aligned component can be found directly, as already mentioned in Section 2.1. (See also Appendix A). It will be noted that no increasing behaviour of H_c with ψ less than 50°–55° can be found, although the particles used here have a small amount of the porosity (see also, [11]).

First, our model based on the interacting SJBCs, which form the regular space lattice, was directly applied to explain quantitatively the behaviour shown in Fig. 8. However, as was shown and suggested in the preceding section, especially in Figs 4–7, no attempts that lead to a definite explanation could be found. Therefore, another type of physical background, which affects the behaviour of the AVH_c measured experimentally, should be found.

One such attempt was made by very careful observations based on TEM images of the powder particles studied here. As is shown by Fig. 9 as an example [7], even if the powder is extremely diluted, local aggregates whose typical form is called "multiple" or "bundle" [17] could easily be found. Furthermore, after submitting a previous paper [7], it was pointed out by Cecchetti [14] that the aggregation of the single-domain particles could be suggested from various types of measurements of the magnetization [18–21]. Therefore, without a loss of generality, it can be assumed that the local aggregates of the multiple type are unavoidably created in any type of assembly of very fine, acicular particles.

According to the results obtained in the preceding section, it was tentatively assumed that, in the system made by a perfectly aligned component and a random component, the former component can be divided into two sub-components: a normally aligned sub-component, and the multiple-type local aggregated sub-component. As the normal sub-component, the isolated SJBCs (which have a packing of 0%) or the finite cluster whose size is specified by (Nx, Ny, Nz) of (10, 10, 10), were taken into account. Also, as the aggregated sub-component, the two-dimensional raft that is defined by $(Nx, 1, 1)$ was assumed, where the various values of Nx were *ad hoc* tested. The packing of the raft to be considered was determined as follows: after our detailed TEM observations on the tape material [4], the fine, acicular particles, of which the raft consists, were usually encapsulated by chemical surfactants and binder resins whose thickness was about

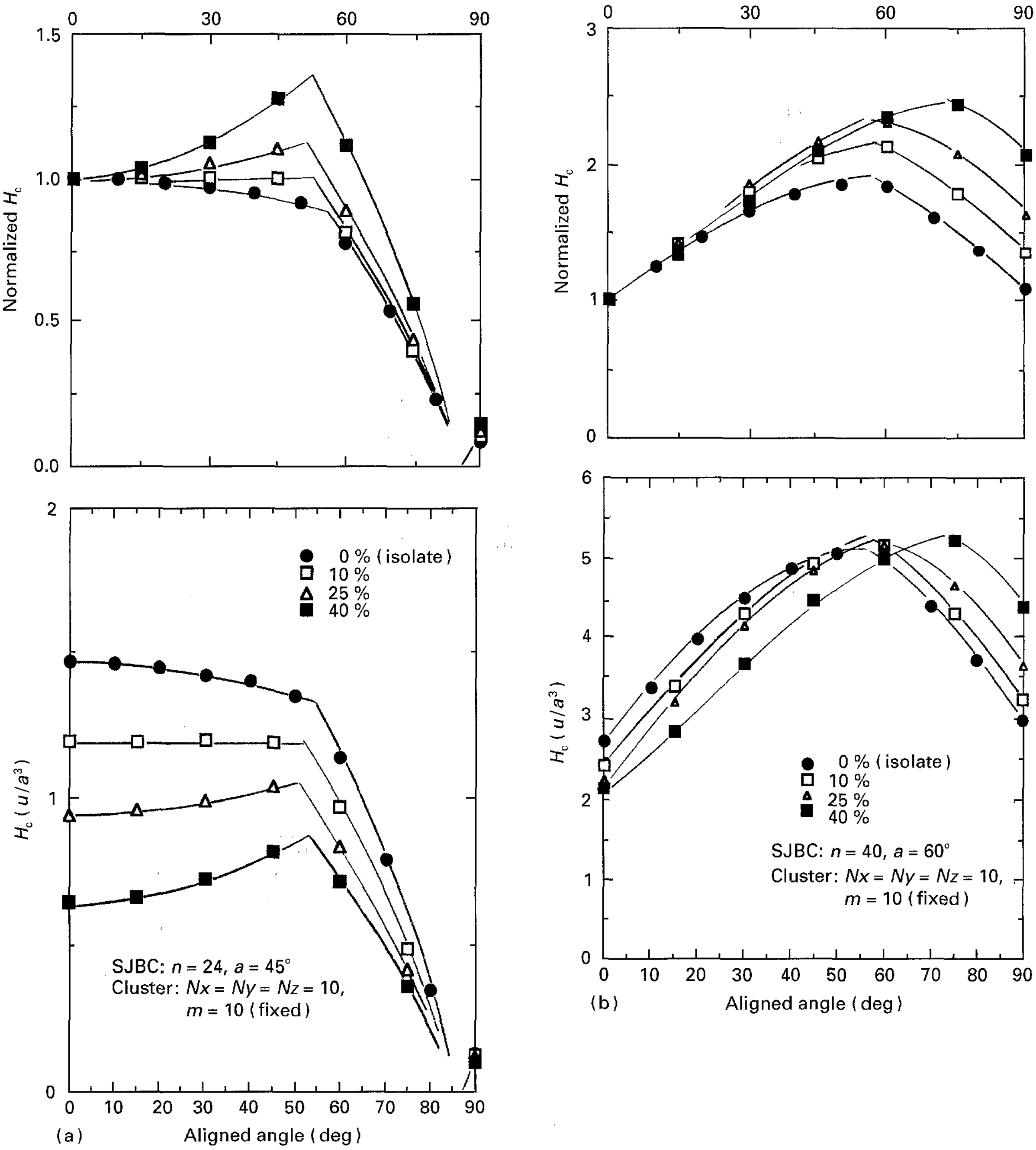

Figure 6 Effect of particle morphology on angular variation of H_c of a finite three-dimensional lattice forming an orthorhombic type. (a) Partially porous particle, (b) "Type-D" particle.

3.5 nm or less. Then, the lower-limit of t, defined in Fig. 1, could be estimated to be about $(20\,\text{nm} + 2 \times 3.5\,\text{nm})/20\,\text{nm} = 1.35$, which leads to a packing of about 85 vol % in the case of the twin-type multiple (it will be noted that the theoretical packing is defined as the closest contact between the particles providing a packing of "100%").

Rigorously speaking, the value of H_c of the system must be estimated numerically from the calculated magnetization hysteresis loop of the system. Here, however, under the assumption of a very small interaction among the constituent components of the system, H_c was directly estimated from a hypothetical linear additivity of the components, see Appendices A and B.

A typical example of the calculated results is shown in Fig. 10, where the system aligns perfectly and consists of a finite cluster of JBCs with (n, α) of (10, 0) having a packing of 10% and a location mode of $m = 10$ under the symmetric fanning mode, and a twin-type multiple of JBC with (n, α) of (10, 0) having a packing of 85% under the modified fanning mode. The calculated AVH_c of the aligned system seems to be enough if the results are applied to the explanation of the AVH_c observed experimentally in the tape materials.

Such trials for the data shown by Fig. 8 were performed and the results obtained are partly given in Table I. For details about the method of estimating the contributions from three constituent components, namely the normal, multiple and three-dimensional randomly oriented components, see Appendices A and B. Table I shows clearly that an extremely large contribution from the multiple component is induced by

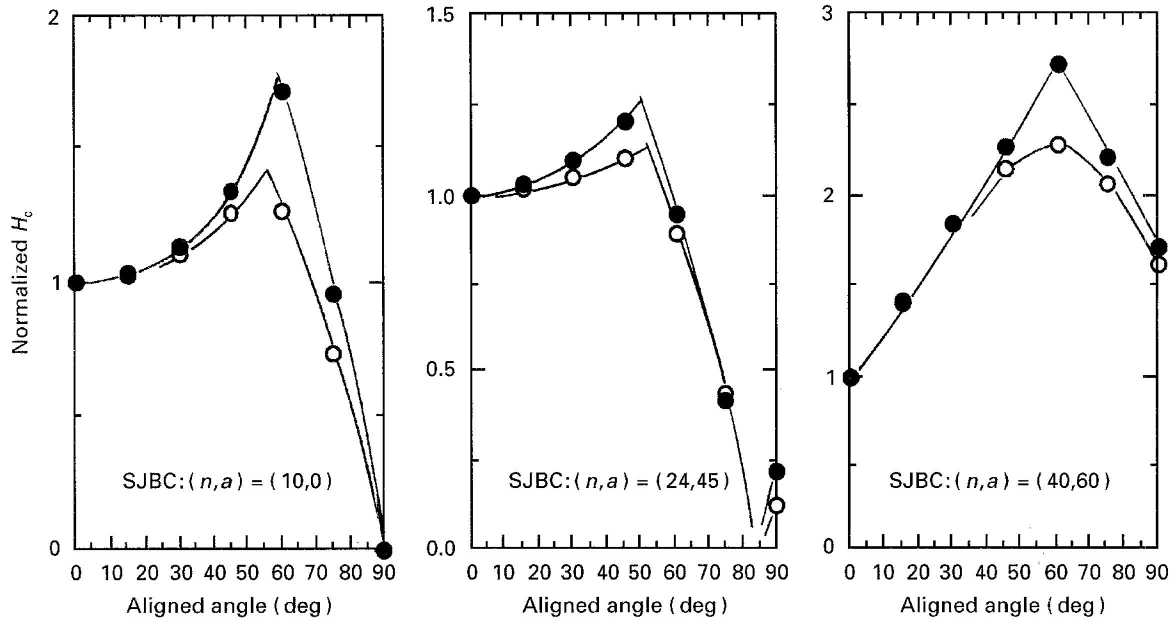

Figure 7 Effect of intraparticle porosity on angular variation of H_c of a finite three-dimensional lattice forming an orthorhombic type. Three types of SJBCs with nearly the same aspect ratio are taken into acount. (○, ●) Normalized H_c for SJBCs (○) without or (●) with pores, represented by introducing dipole-less unit-spheres.

increasing the packing of the system. If it is assumed that the experimentally determined packing p, equals the theoretically defined packing, ρv, as shown by the two solid lines in Fig. 8, two experimentally observed AVH_c at the different packing densities can be explained by the results shown in Table I.

It seems that the system made from very fine, acicular particles with finite packing, unavoidably includes local aggregates such as the multiples.

4.2. Application to published data

As was mentioned in Section 2, AVH_c of systems made from various types of fine, acicular particles have been reported by many researchers interested in the read/write characteristics of magnetic recording media. Here, the results of our model developed in the preceding section are reported.

4.2.1. System made from the acicular particles of γ-Fe_2O_3

First, the experimental results reported by Richards [8] were investigated. He studied the effect of the packing on the angular variation of the reduced H_c obtained for acicular particles of γ-Fe_2O_3, to show that the experimental angular variation of the reduced H_c of the system deviates from that predicted by the Jacobs-Bean's CSFM, if the system packing is larger than about 20 vol %.

Based on our model of this system, it is clearly shown that this deviation is due to (1) the low orientability of the particles because of their low acicularity; (2) the co-existence of the three-dimensional randomly oriented component, and (3) the unavoidable co-existence of the multiple component. Table II shows our trial result of the component analysis of the system treated by Richards where the three-dimensional oriented component of 90 vol % is tentatively assumed. As is shown in Fig. 11, our treatment can explain the results of Richards [8].

Secondly, the behaviour of the AVH_c observed in three audio tapes made from three kinds of fine acicular particles of γ-Fe_2O_3 reported by Cecchetti *et al.* [11] was considered. They used three audio tapes (samples A, B and C) that provide the best high dynamic, average and standard low-noise quality as an acoustic performance, respectively, to show three angle-dependences of H_c quite different from that predicted by the coherent reversal mode of the magnetization for single domain particles (Fig. 12a). The uniformity of the elongation (or "aspect ratio"), shape and size of the particles of which tapes A, B and C are made up, is reported to decrease in the order A > B > C. Based on measurements of the rotational hysteresis loss as a function of applied field for each tape and from TEM images of the particles used, they have concluded that a kind of CSFM must be involved in the system. Therefore, an approach by the CSFM will be necessary to reproduce correctly the three experimental AVH_c.

The results obtained are given in Table III and are shown in Fig. 12b–d, where the solid lines denote the resultant AVH_c based on our component analysis. It was suggested that both samples A and C contain, as the perfectly aligned component, about 55 vol % finite cluster of the normal component and about 45 vol % twin bundle of the multiple component. Therefore, the higher performance in sample A than in C can be partly caused by the higher value of H_c (and maybe the higher value of the squareness ratio) of the sample A. On the other hand, in sample B, which shows a medium quality, the existence of a finite cluster of about 80 vol % as the perfectly aligned normal component

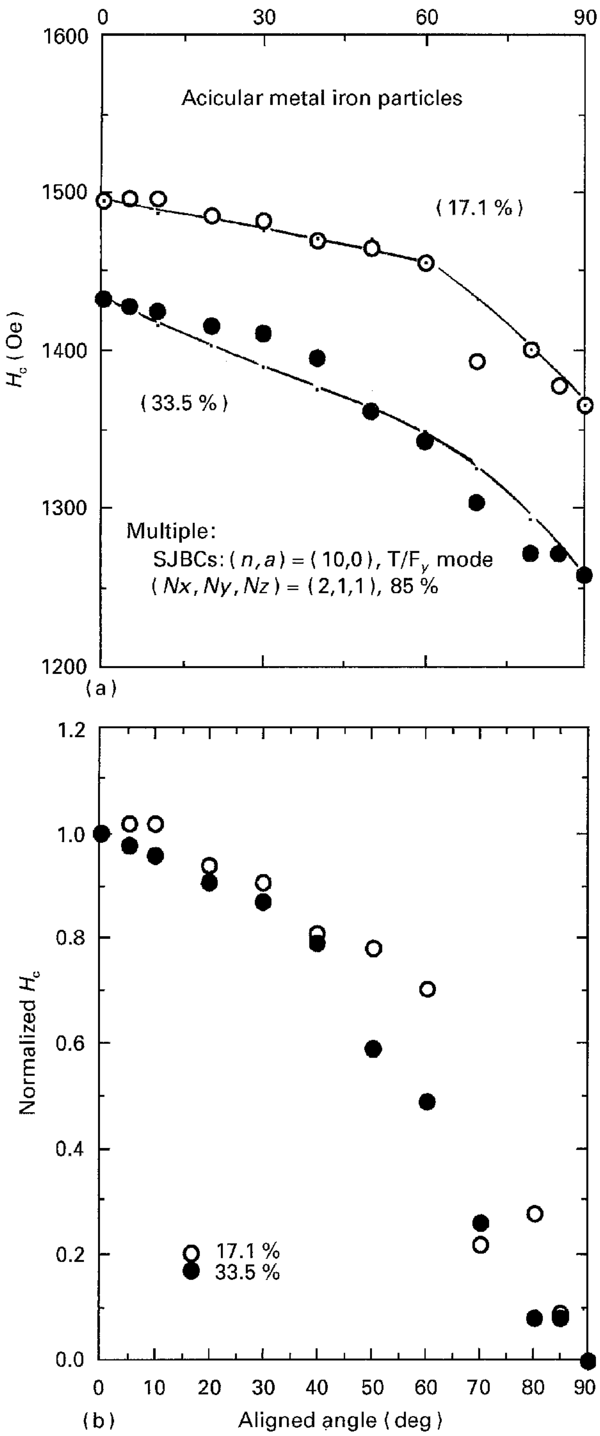

Figure 8 Experimentally observed angular variations of H_c showing a typical effect of packing degree of acicular particles of α-Fe in two nominally uni-axially oriented tape materials. In (a), solid lines show simulation results.

Figure 9 A typical TEM image showing the unavoidable co-existence of local aggregates of multiple-type just like a "raft" found among "normal" acicular particles. Published by permission of Chapman and Hall Ltd.

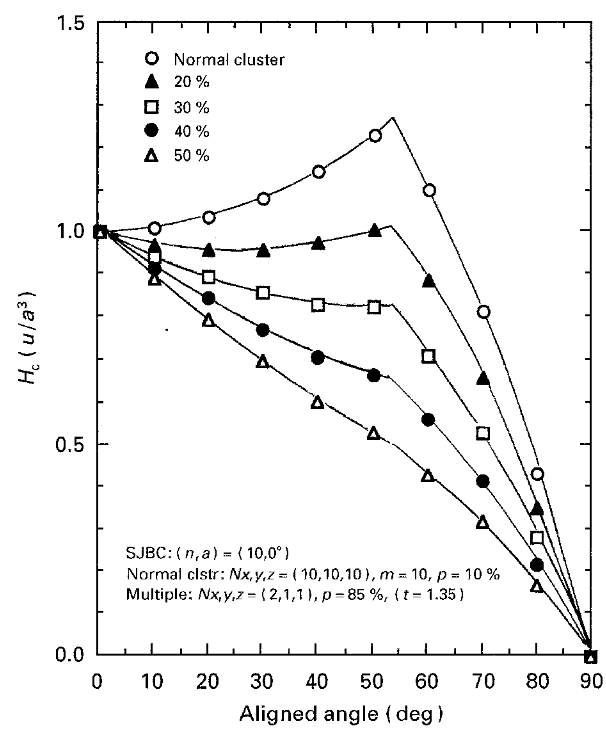

Figure 10 Effect of packing on the angular variation of H_c for a multiple-containing uni-axially oriented system. A finite cluster forming a regular space lattice like an orthorhombic type as a normal component and a twin-type bundle as a multiple component, are taken into account.

was found. If the physical properties of the tape, such as the surface roughness, the remanent magnetization and the squareness are known, it will be possible to investigate more precisely the relation between the particle morphology and the acoustic performance of the tape.

4.2.2. System made from the acicular metallic particles

In this section we first re-examine the experimental effect of the packing on the AVH_c observed in three

TABLE I Result of component analysis on two nominally uni-axially oriented tape materials made with very fine, acicular particles of α-Fe[a]

System packing (vol %)	Perfectly aligned component (vol %)			Randomness (vol %)	
	Normal component[b]		Multiple component, twin bundle[d]	Three-dimensional[e]	Packing[f]
	Isolate[b]	Finite cluster[c]			
17.1	10.8	–	4.1	85.1	16.0
	–	10.9	4.0	↑	14.8
33.5	12.7	–	10.3	77.0	32.2
	–	12.9	10.1	↑	30.6

[a] Their particle morphology can be classified into "Type-S".
For details of the estimation method on the component analysis, see Appendix A.
[b] Non-defective SJBC with (n, α) of (10, 0) under D/Fx(symmetric fanning) mode is assumed to be available.
[c] Assumed data are as follows:
Constituent JBC: (n, α) = (10, 0), not defective
Size : (Nx, Ny, Nz) = (10, 10, 10)
Packing density : ρv = 10 vol %
Location mode : m = 10
Reversal mode : D/Fx (symmetric fanning in dimer unit).
[d] Assumed data are as follows:
Constituent JBC: (n, α) = (10, 0), not defective
Size : (Nx, Ny, Nz) = (2, 1, 1)
Packing density : ρv = 85 vol %
Reversal mode : T/Fy (modified symmetric fanning in tetramer unit).
[e] Value estimated from squareness of magnetization loop. See Appendix B.
[f] Simulated value of packing degree that satisfies the system packing.

TABLE II Simulating results on the published data. 1. Effect of packing load on the angular variation of H_c for acicular particles of γ-Fe_2O_3 reported by Richards [9][a]. The value of g was assumed to be 0.1

System packing (vol %)	Perfectly aligned component (vol %)			Randomness (vol %)	
	Normal component[b]		Multiple component, twin bundle[d]	Three-dimensional[e]	Packing[(f)]
	Isolate[b]	Finite cluster[c]			
12.2	9.9	–	0.1	90.0	13.5
21.5	–	8.5	1.5	↑	21.6
35.0	–	7.0	3.0	↑	35.3

[a] The particles used are not smooth elipsoids and are reported to have a mean length of 0.7 μm and a mean aspect ratio near 5.
[b–f] See the footnotes b–f of Table I.

systems made from the famous elongated single-domain iron-particles prepared by electrodeposition into mercury, followed by an annealing process [10]. Luborsky and Paine [10] had used a "physical" model of domain structures of hypothetical particles and assemblies, made from "unoriented barium-ferrite small magnets" that were assumed to play the role of unit spheres in the chain-of-spheres, to interpret "experimentally" the observed results that are re-plotted in Fig. 13a.

However, it now becomes possible to explain, quantitatively their results if our method of the component analysis of the system is adapted as follows. As is shown in Table IV, the system with the packing of 8 vol % can consist of only the isolated SJBC having (n, α) of (10, 0) as the completely aligned component. No multiple component can be included in this system. On the other hand, both the systems with a packing of 35 and 47 vol % can include the twin-type multiple as the completely aligned component of about 15 vol %. The essential difference between the two systems is due to the packing state of the three-dimensional random component, see Table IV. Therefore, the applicability of our method of the component analysis of the system consisting of fine acicular particles will be shown for the well-known system of elongated single-domain particles of iron.

The second case is the quantitative interpretation of the AVH_c observed for fine cylindrical nickel particles. Kaneko [12] prepared nickel alumite films by the electrodeposition into microscopic pores of anodic oxidized aluminium followed by heat treatment, to investigate the reversal mechanism of the magnetization. He concluded that his experimental results could be explained by the CSFM after the observation of the particle morphology by TEM and also measurements of the coercive force, the anisotropy field, the rotational hysteresis loss and the nucleation field. In order to obtain his conclusion, he noted especially the angular variation of the nucleation field for the

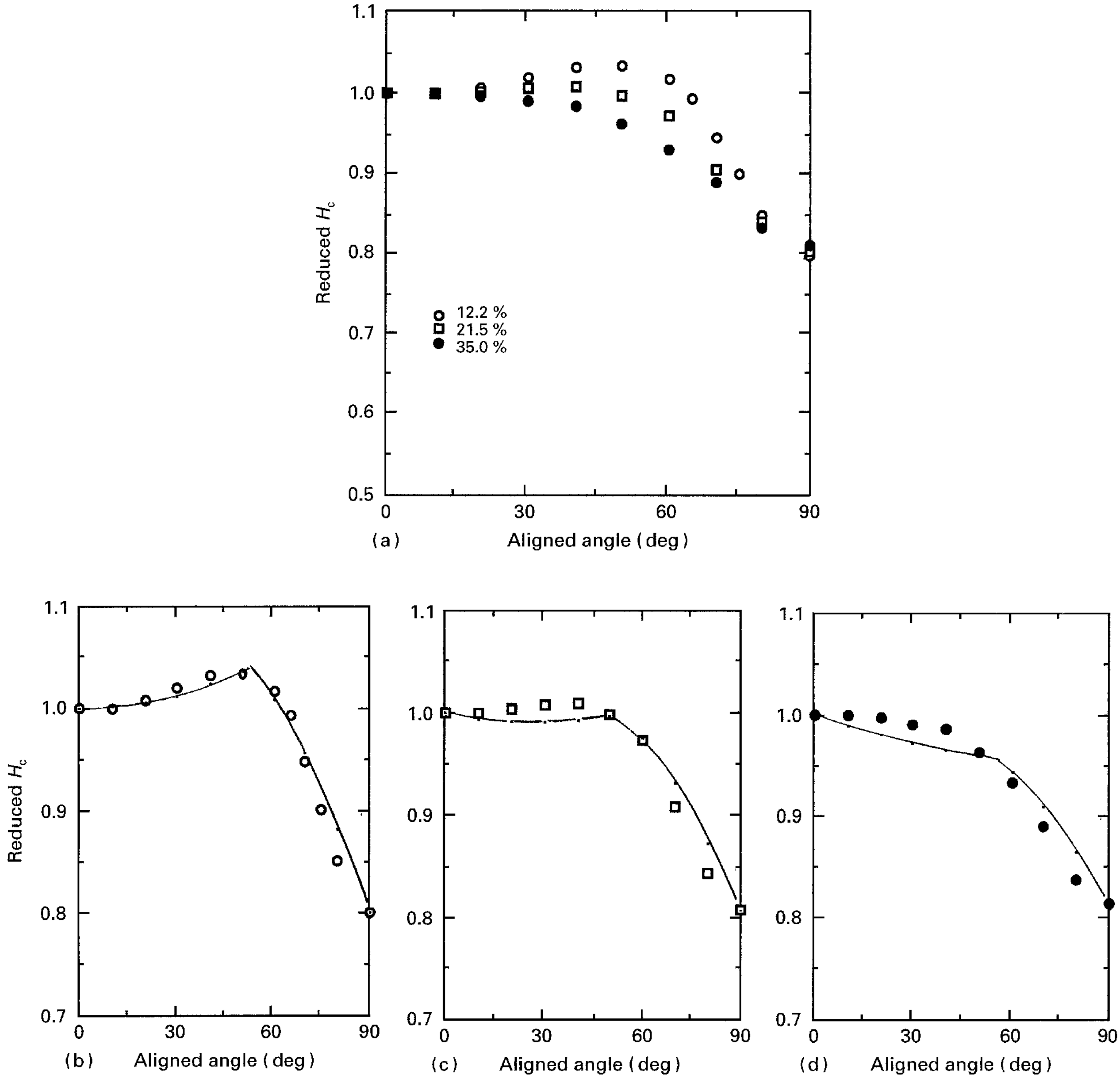

Figure 11 Application to published angular variation of H_c. (a) Acicular particles of γ-Fe_2O_3 reported by Richards [9]. Published by permission of the American Institute of Physics. (b) 12.2 vol %, (c) 21.5 vol %, (d) 35.0 vol %.

annealed sample and the angle dependence of H_c, namely that a maximum H_c was found at the easy direction of the magnetization (Figs 3 and 2 of [12], respectively).

Hence, a possible explanation of the AVH_c for the as-grown and also as-annealed nickel alumite films should be obtained in the framework of the CSFM. It would be possible if the amounts of the isolated SJBC and the twin-type multiple as the completely aligned component were assumed to be about 61% and 14% for the former sample and about 48% and 30% for the latter sample, respectively, see, Table V and Figs 14a–c. As shown in Fig. 14a, the value of H_c along the easy direction of the magnetization of the sample has slightly increased during annealing. The amount of the twin-type multiple component has increased by about 16% during annealing and the three-dimensional randomly packed component of the samples before and after annealing is evaluated to be almost the same. Because the annealing process can accelerate the aggregation of the particles (which leads generally to decreasing H_c if the annealing is "strong") and also the pore annihilation with re-crystallization (which always leads to increasing H_c if carried out before sintering), it might be possible to conclude that, in the heat treatment for the nickel alumite film carried out by Kaneko, the effect of the pore annihilation on H_c had overcome that of the aggregation of the nickel particles.

The third case was the interpretation of the AVH_c of sputtered films made from Co(host metal)–Cr(guest metal) alloy suitable for perpendicular media of very high-density magnetic recording. Barbero *et al.* [21] prepared various Co–Cr alloy films by r.f. sputtering to investigate the reversal mechanism of the magnetization. As is now well-known, this type of film consists of fine, acicular columns that are mainly aligned perpendicular to the substrate surface. Based on the

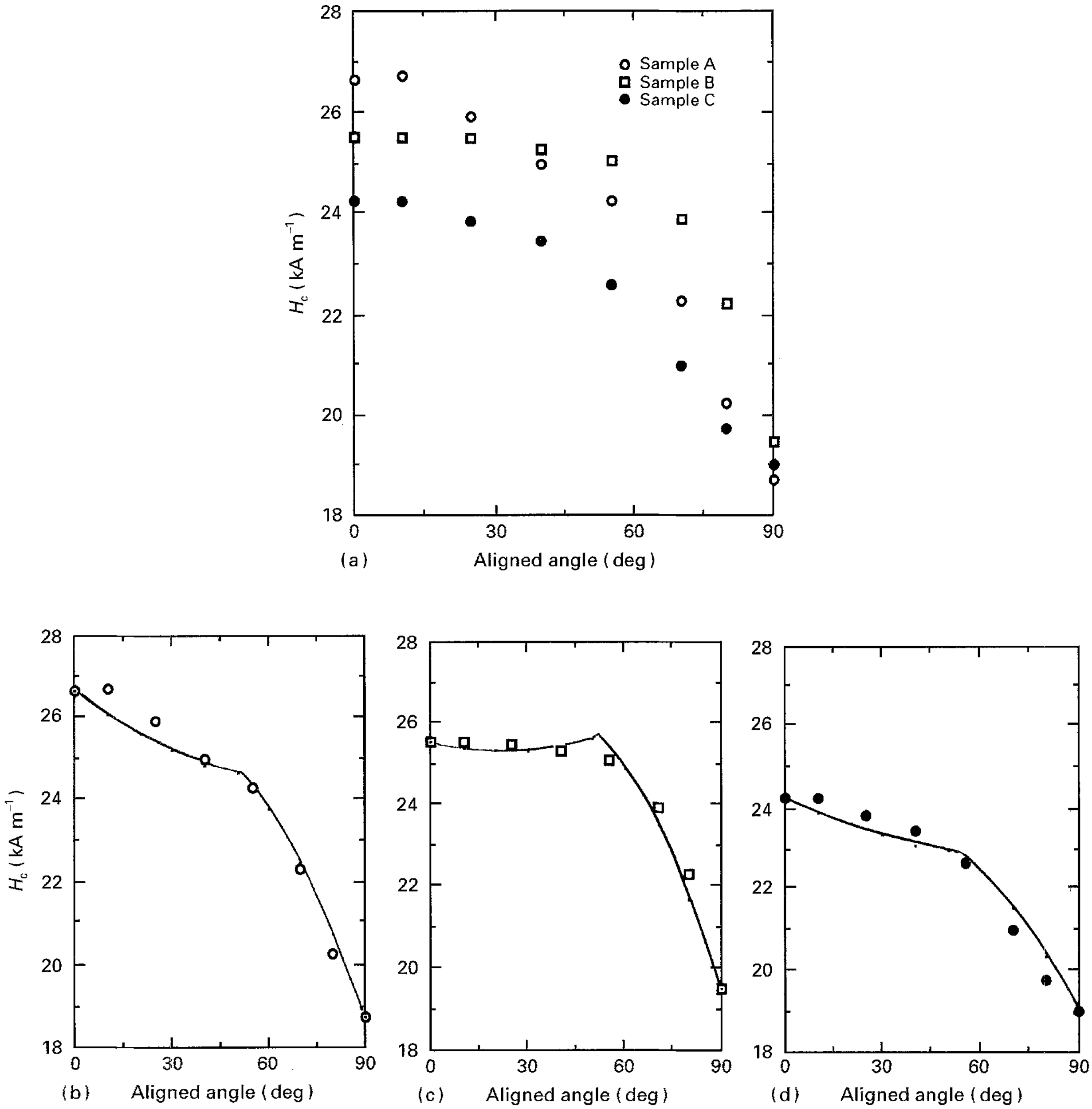

Figure 12 Application to published angular variation of H_c. (a) Acicular particles of γ-Fe_2O_3 reported by Cecchetti *et al.* [11]. They showed that three audio tapes (Samples A, B or C) provide the best high-dynamic, average and standard low-noise quality as an acoustic performance, respectively. Published by permission of the American Institute of Physics. (b) Sample A, (c) Sample B, (d) Sample C.

shape of the rotational hysteresis loss as a function of the internal rotating field, the value of the rotational hysteresis integral, and especially the angular variation of H_c and also of the remanent coercivity, they had suggested that the coherent rotation mechanism is available for the reversal of the magnetization. They had also pointed out the important role of the inter-columnar interaction and the amount of structural anomalies in the columns.

The experimentally observed AVH_c, showing a maximum value along the easy direction of the magnetization, can be reproduced by our method of the component analysis based on the CSFM. In Fig. 15a, samples A1 and A2 with the same alloy component (22.19 wt % Cr) show a different AVH_c, although they have nearly the same values of H_c along the easy and also the difficult direction of magnetization. A main difference between A1 and A2 may be the width of the columns of which the films consist (Table of [20]). The ensemble structure of the columns in sample B1 (17.01 wt % Cr) in Fig. 15a is coarser than those of samples A1 and A2. This sigmoidal behaviour of the AVH_c is one of the reasons why the coherent rotation mechanism is available in sputtered films.

According to our method of component analysis of the system, it is possible to fit the experiments by the CSFM, if the finite-sized cluster as the normal component and the twin-type multiple are assumed to be contained as is shown in Table 6, see Fig. 15b–d. It will be noted that, to reproduce quantitatively the experimental behaviour of sample B1, it was necessary to assume that the twin-type multiple had a packing fraction of 50 vol %, as reflecting the aggregation degree of the columns.

TABLE III Simulating results on the published data. 2.1 Component analysis of Audio-use tapes made from three kinds of acicular particles of γ-FeO_2O_3 reported by Cecchetti *et al.* [11]

Samples	Perfectly aligned component (relative vol %)			Notes (tape-quality reported)
	Normal component[a]		Multiple, component, twin bundle[c]	
	Isolate[a]	Finite cluster[b]		
A	–	54.3	47.5	Best high dynamic
B	–	80.0	20.0	Average quality
C	–	55.4	44.5	Standard low noise

[a–c] See footnotes b–d of Table I.

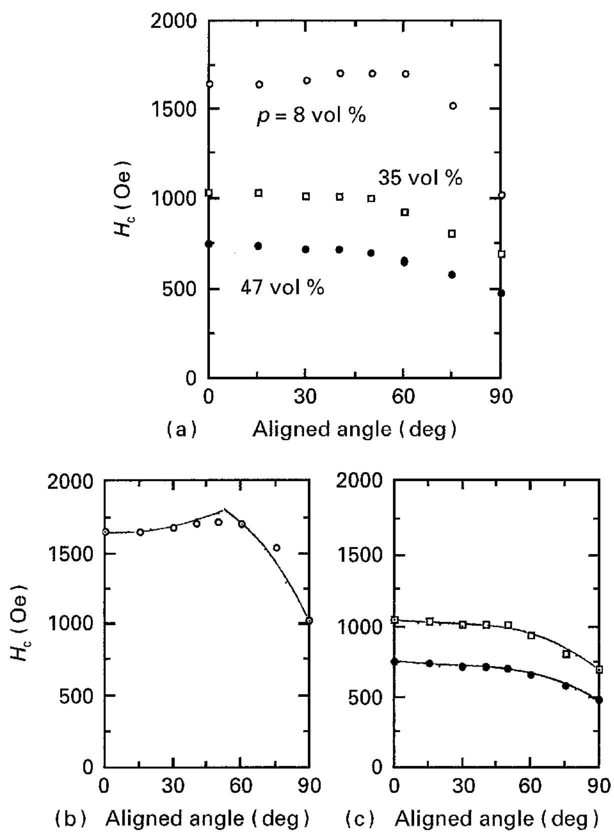

Figure 13 Application to published angular variation of H_c. (a) Acicular particles of α-Fe reported by Luborsky and Paine [10]. Published by permission of the American Institute of Physics. (b) $p = 8$ vol %, (c) $p =$ (□) 35 vol %, (●) 47 vol %.

The fourth case was the very fine acicular particles of α-iron whose morphology can be represented by the chain-of-spheres with the pores. Bottoni *et al.* [22] investigated, systematically and experimentally, the magnetization mechanism of α-iron particles with the above-mentioned morphology [13, 19, 22]. In particular, they had found that the AVH_c is very different from that due to the CSFM, even if the system is extremely diluted, such as a packing fraction of about 0.1 vol % (Fig. 1 of [13]). They concluded that one of the reasons is the inter-sphere necking in the chain-of-spheres.

Based on the component analysis method developed here, an additional possibility that can partly explain experimental behaviour of the AVH_c is now presented. Our tentative result is shown by Table VII and Fig. 16, where the effects of the intersphere necking and the pores in the chain on the AVH_c are neglected, in order to simplify the present problem. As was already pointed out by Bottoni *et al.* [22], even in the diluted system, it is seemed to be very likely that the twin type of multiple can persist as local aggregates in the system consisting of very fine acicular particles of α-iron whose morphology can be geometrically represented by the chain-of-spheres. Therefore, the quantitative effect of the intersphere necking in the chain will be the next most important problem. Such investigations are now under way and the results will be reported in the near future.

5. Conclusions

As the second part of our programme of investigations on the many-body effects of the interacting fine acicular particles with various types of the morphology on the reversal of the magnetization of the system, in order to study the interparticle-interaction effect on the angular variation of H_c, an extended chain-of-

TABLE IV Simulating results on the published data. 3. Effect of packing load on the angular variation of H_c for acicular particles of α-Fe reported by Luborsky and T. O. Paine [9]. The values of g were estimated from their observed values of the squareness data

System packing (vol %)	Perfectly aligned component (vol %)			Randomness (vol %)	
	Normal component[a]		Multiple component, twin bundle[c]	Three-dimensional[d]	Packing[e]
	Isolate[a]	Finite cluster[b]			
8	65.3	–	–	23.1	34.7
35	–	27.4	14.6	58.0	34.2
47	–	24.6	15.5	59.9	52.3

[a–e] See footnotes b–f of Table I.

TABLE V Simulating results on the published data. 4. Effect of annealing on the angular variation of H_c for "Perpendicular columnars" in nickel alumite film reported by Kaneko [12]. The values of g were estimated from his observed values of the squareness data.

Samples	Perfectly aligned component (vol %)			Randomness (vol %)	
	Normal component[a]		Multiple component, twin bundle[c]	Three-dimensional[d]	Notes[e]
	Isolate[a]	Finite cluster[b]			
A	60.7	–	14.1	25.2	As-grown
B	47.9	–	29.6	22.5	After annealing

[a–e] See footnotes b–f of Table I.

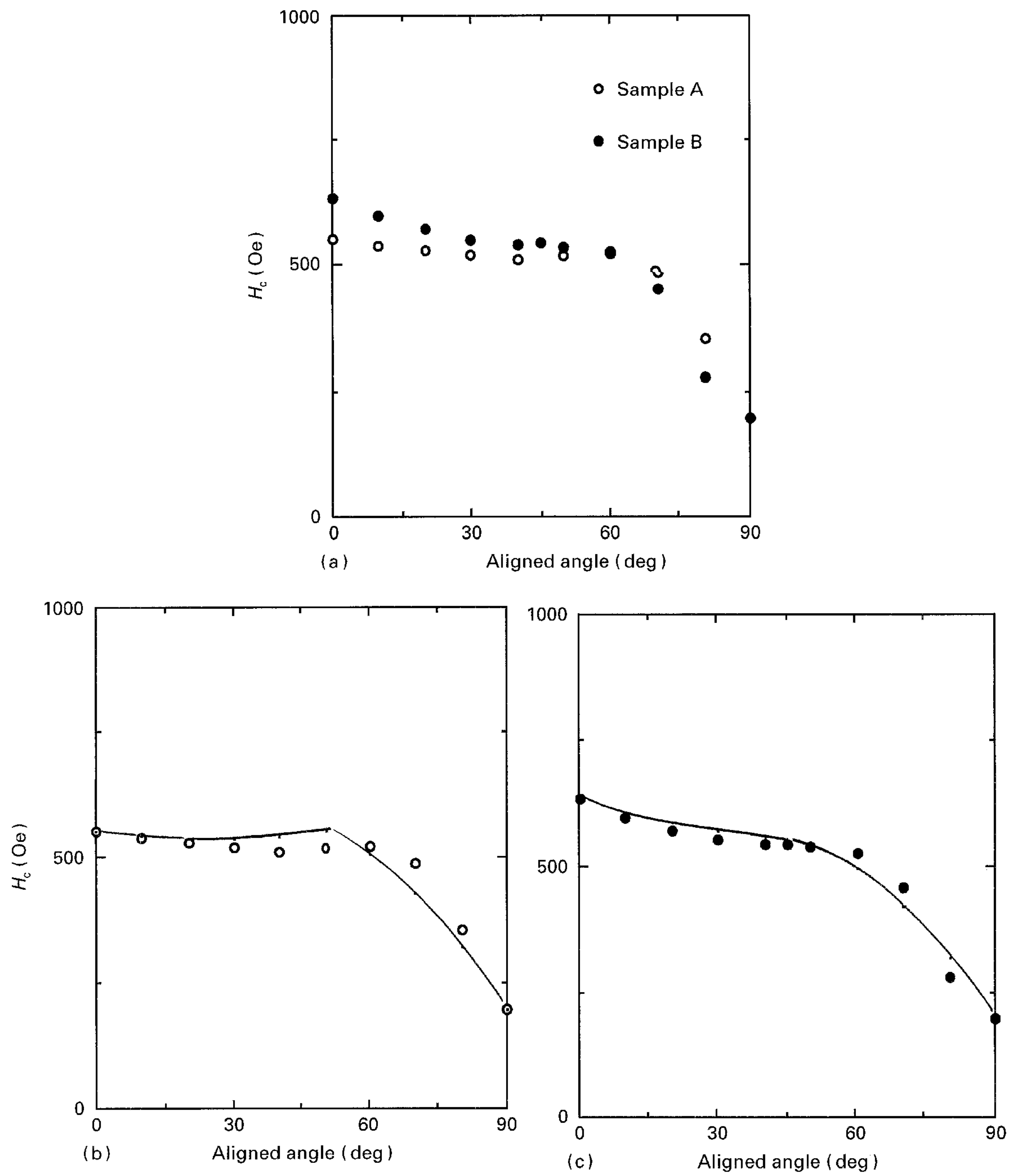

Figure 14 Application to published angular variation of H_c. (a) Nickel alumite films reported by Kaneko [12] who prepared Sample B to investigate the effect of annealing for as-grown sample A. Published by permission of the Institute of Electrical and Electronics Engineers. (b) Sample A, (c) Sample B.

spheres fanning mechanism, CSFM, renewed by the author, but starting from the original Jacobs and Bean model, was directly applied to the interacting chains that form a regular orthorhombic-like space lattice and take the collective reversal of the magnetization.

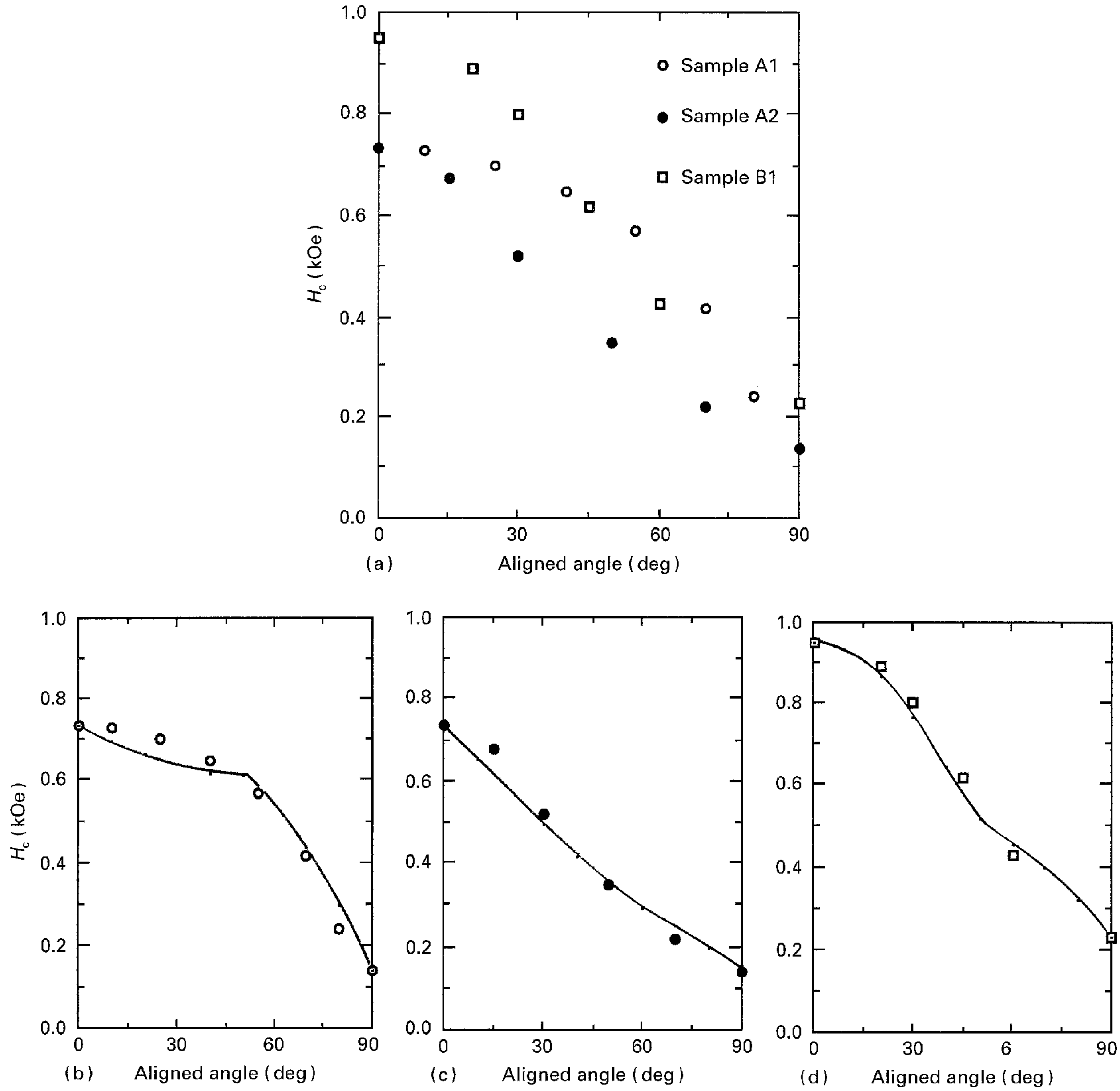

Figure 15 Application to published angular variation of H_c. (a) R.f.-sputtered Co–Cr "perpendicular" columnar particles given by Barbero *et al.* [21], who reported that columnar structure in Samples A1 and A2 is of a dense type, while in Sample B it is a coarse one. Published by permission of the Institute of Electrical and Electronics Engineers. (b) Sample A1, (c) Sample A2, (d) Sample B1.

TABLE VI Simulating results on the published data. 5. Effect of particle morphology on the angular variation of H_c for "perpendicular columnars" in r.f.-sputtered Co–Cr films reported by Barbero *et al.* [21]. Because the squareness data had not been shown by Barbero *et al.*, the values of g could not be estimated

Sample	Perfectly aligned component (relative vol %)			Notes on (columnar structure)
	Normal component[a]		Multiple, component, twin bundle[c]	
	Isolate[a]	Finite cluster[b]		
A1	–	58.6	41.4	Dense columnar
A2	–	16.8	83.2	Dense columnar
B	–	29.0[d]	71.0	Coarse columnar

[a–c] See footnotes b–d of Table I.
[d] Only in this case, to fit the experiment, the packing degree was assumed to be about 50 vol %.

The angular dependency of H_c is hardly affected by the interaction between the particles *except* in the case where the chains form a multiple type of local aggregates. In other words, only the lateral interaction, namely the interaction across the chains, will exhibit a monotonically decreasing angular variation of H_c.

TABLE VII Simulating results on the published data. 6. Effect of particle aggregation on the angular variation of H_c for fine acicular particles of α-Fe reported by Bottoni *et al.* [22]. Because the squareness data were not reported in [22], the values of g could not be estimated

Sample	Perfectly aligned component (relative vol %)			Notes on particle aggregation
	Normal component[a]		Multiple, component, twin bundle[c]	
	Isolate[a]	Finite cluster[b]		
$p \simeq 0.1\%$	71.1	–	28.9	Extremely diluted
Tape	49.7	–	50.3	in tape material

[a–c] See footnotes b–d of Table I. However, in these cases, the packing of the twin-type multiple was assumed to be about 70 vol %.

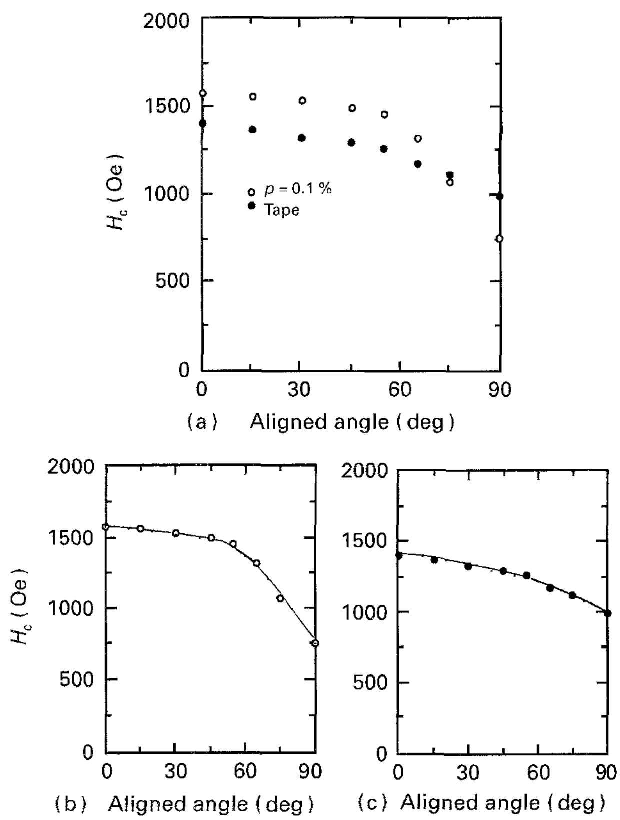

Figure 16 Application to published angular variation of H_c. (a) Acicular particles of α-Fe reported by Bottoni *et al.* [22]. Published by permission of Elsevier Science Publishers. (b) $P = 0.1$ vol %, (c) tape.

Remembering the results obtained in the first part of our investigations concerning the above mentioned field of the magnetization, that the lateral interaction is basically a strong physical source providing the decreasing behaviour of H_c with the packing degree of interacting particles system [4], this type of magnetic interaction will essentially play a most important role in the various magnetic properties of the system.

In the experimentally observed angular variations of H_c, the maximum value of H_c can often be found at the easy direction of magnetization. This behaviour has sometimes led to the conclusion that the coherent rotation or an incoherent reversal other than the symmetric fanning, is dominant in the system. However, the present study suggests that a monotonically decreasing type of angular variation of H_c can be due to the CSFM, if the system includes, for example, the twin type of multiple. Because, in many cases, the co-existence of the multiple of local aggregates can be unavoidable in a system where the fine acicular particles interact with each other, it is important to clarify the physical role of such a morphological property in the rotational integral or the rotational hysteresis loss whose experimental values are often reported in the published data. Furthermore, investigation of the effect of removing the local aggregates such as the multiples from the system, on the read/write characteristics, will be important in revealing the advanced properties of the magnetic media.

Acknowledgements

The author thanks the Director and the Deputy of the Central Research Institute of Mitsui Toatsu Chemicals, Inc., Messrs T. Takase and N. Itoh, respectively, for their continuous support and permission to publish this work. He also acknowledges the valuable advice about the important role of the local aggregates in the reversal of the magnetization in the interacting fine acicular particles system and the encouragement of Professor A. Cecchetti, Department of Physics, Ferrara University, INFM, Ferrara, Italy.

References

1. T. TAGAWA, K. SUDOH, S. TAKAHASHI, M. MATSUNAGA and KZ. OHSHIMA, *IEEE Trans. Magn.* **MAG-21** (1985) 1492.
2. KZ. OHSHIMA, *ibid.* **MAG-22** (1986) 726.
3. *Idem, ibid.* **MAG-23** (1987) 2826.
4. *Idem, J. Magn. Magn. Mater.* **79** (1989) 276.
5. *Idem, J. Assoc. Mater. Eng. Resources* **3** (1990) 7 (*Sozai-Busseigaku Zasshi*, in Japanese).
6. I. S. JACOBS and C. P. BEAN, *Phys. Rev.* **100** (1955) 1060.
7. KZ. OHSHIMA, *J. Mater. Sci. Lett.*, in press.
8. D. B. RICHARDS, in "AIP. Conference Proceedings" (MMM'71), Vol. 5 (1972) p. 926.
9. I. S. JACOBS and F. E. LUBORSKY, *J. Appl. Phys.* **28** (1957) 467.
10. F. E. LUBORSKY and T. O. PAINE, *ibid.* **31** (1960) 66S.
11. A. CECCHETTI, A. R. CORRADI and G. FAGHERAZZI, *IEEE Trans. Magn.* **MAG-16** (1980) 86.
12. M. KANEKO, *ibid.* **MAG-17** (1981) 1468.
13. G. BOTTONI, D. CANDOLFO, A. CECCHETTI, A. R. CORRADI and F. MASOLI, *J. Magn. Magn. Mater.* **104-107** (1992) 961.
14. A. CECCHETTI, *private communication*, 19 July 1993.

15. E. C. STONER and E. P. WOHLFARTH, *Philos. Trans. R. Soc.* **240** (1948) 599.
16. W. K. GRIMWOOD, J. R. HORAK, H. J. KRALL and R. J. DELMORE, *IEEE Trans. Magn.* **MAG-31** (1967) 49.
17. J. E. KNOWLES, *ibid.* **MAG-17** (1981) 3008.
18. G. BOTTONI, D. CANDOLFO, A. CECCHETTI and F. MASOLI, *ibid.* **MAG-8** (1972) 770.
19. G. BOTTONI, D. CANDOLFO, M. CECCHETTI, A. R. CORRADI and F. MASOLI, *J. Magn. Magn. Mater.* **120** (1993) 167.
20. G. BOTTONI, *J. Appl. Phys.* **69** (1991) 4499.
21. C. BARBERO, G. BOTTONI, P. BUTTAFARA, D. CANDOLFO, A. CECCHETTI, F. MASOLI, M. PIANO and C. SALUSTRI, *IEEE Trans. Magn.* **MAG-18** (1982) 1104.
22. G. BOTTONI, D. CANDOLFO, A. CECCHETTI and F. MASOLI, *J. Magn. Magn. Mater* **116** (1992) 285.

Received 24 March 1994
and accepted 22 June 1995

Appendix A. Component analysis method using the system H_c

A *semi-quantitative* method is shown of estimating the constituent components in a system made from a perfectly aligned and randomly oriented component.

After Jacobs and Luborsky [9], we denote the volume fraction of the perfectly aligned component of the system by g. As a first approximation, we assume that the coercivity of the system has a linear additivity about the constituent components. Then, H_c of the system can be represented as

$$H_c(\psi, g) = g H_c^{(or)}(\psi) + (1-g) H_c^{(rnd)} \quad (A1)$$

where $H_c^{(or)}$ and $H_c^{(rnd)}$ denote the coercivity of the perfectly aligned and the randomly oriented components, respectively. In Equation (A1), we have

$$H_c^{(or)} = 0 \quad (A2)$$

at $\psi = 90°$ (perpendicular direction) and $H_c^{(rnd)}$ is isotropically constant. Therefore, the normalization representation that is used in the text becomes

$$[H_c(\psi, g) - H_c(\psi = 90°, g)]/[H_c(\psi = 0°, g) - H_c(\psi = 90°, g)] = H_c^{(or)}(\psi)/H_c^{(or)}(\psi = 0°) \quad (A3)$$

which leads to the reduced form of the angular variation of H_c of the perfectly aligned component.

Next, after the discussion given in the text, we divide this perfectly aligned component of the system into two sub-components, which are a normal component and a multiple-like locally aggregated component, whose relative volume fractions are given by $f^{(or-n)}$ and $f^{(or-m)}$, respectively

$$H_c^{(or)}(\psi) = f^{(or-n)} H_c^{(or-n)}(\psi) + f^{(or-m)} H_c^{(or-m)}(\psi) \quad (A4a)$$

where

$$f^{(or-n)} + f^{(or-m)} = 1 \quad (A4b)$$

and $H_c^{(or-n)}$and $H_c^{(or-m)}$ denote the coercivity of the normal and multiple-type locally aggregated sub-components, respectively. Furthermore, if we represent the right-hand side of Equation A3 by the reduced forms of $H_c^{(or-n)}$ and $H_c^{(or-m)}$ as follows

$$H_c^{(or)}(\psi)/H_c^{(or)}(\psi = 0)° = fn[H_c^{(or-n)}(\psi)/H_c^{(or-n)}(\psi = 0)°] + fm[H_c^{(or-m)}(\psi)/H_c^{(or-m)}(\psi = 0)°] \quad (A5a)$$

where

$$fm + fn = 1 \quad (A5b)$$

then, for example, $f^{(or-n)}$ can be related to fn by the following equation

$$f^{(or-n)} = 1/[1 + \{H_c^{(or-n)}(\psi = 0°)/H_c^{(or-m)}(\psi = 0)°\} \times (1/fn - 1)] \quad (A6)$$

In the case of the iron particles with packing fraction 17.1 vol % discussed in the text, if we take an isolated JBC with (n, α) of (10, 0) under the D/Fx mode [2] as the normal sub-component and if we assume the twin-type multiple under the T/Fy mode [2] as the local aggregated sub-component of the perfectly aligned component, respectively, the numerical values of fn, $H_c^{(or-n)}$ ($\psi = 0$), $H_c^{(or-m)}$ ($\psi = 0$) were 0.627, 2.5315 and 4.0165, respectively. Then, we obtain the values of $f^{(or-n)}$ and $f^{(or-m)}$ of 0.727 and 0.273, respectively. Because, in this case, as given in Appendix B, the value of g could be estimated to be about 0.149, the system investigated here can be made from the normally aligned, locally aggregated aligned and three-dimensionally oriented components of $0.149 \times 72.7 = 10.8$ vol %, $0.149 \times 27.3 = 4.1$ vol %, and 85.1 vol %, respectively.

Strictly speaking, Equation A1 does not hold. The magnetization can have a linear additivity about the constituent components only if the magnetic interactions among these components are negligibly small. A more quantitative component analysis can be made by computing H_c directly from the calculated magnetization curve of the system made from perfectly aligned and randomly oriented components. Such calculations are now under way. The results will be reported in the near future.

Appendix B. Estimating the factor g

Jacobs and Luborsky [9] have proposed a way to estimate the factor g of the system made from the perfectly aligned and randomly oriented components, which uses the observed ratio of the remanence to the saturation magnetization. Here, we follow this simple idea for convenience. If the squareness of the magnetization loop of the system has a linear additivity about the constituent components, it can be represented as

$$SQ(\psi, g) = g\, SQ^{(or)}(\psi) + (1-g) SQ^{(rnd)} \quad (A7)$$

where SQ, $SQ^{(or)}$ and $SQ^{(rnd)}$ denote the squareness of the system, the perfectly aligned and the randomly oriented components, respectively. In Equation A7

$$SQ^{(or)} = 1 \quad \text{at } \psi = 0° \text{ (parallel direction)} \quad (A8a)$$

$$= 0 \quad \text{at } \psi = 90° \text{ (perpendicular direction)} \quad (A8b)$$

$SQ^{(\mathrm{rnd})}$ is isotropically constant, and if the randomized component is three-dimensional, then

$$SQ^{(\mathrm{rnd})} = 1/2 \tag{A9}$$

Then, Equations A7–A9 lead to

$$SQ(\psi = 0°, g) = (1 + g)/2 \tag{A10a}$$

and

$$SQ(\psi = 90°, g) = (1 - g)/2 \tag{A10b}$$

From Equations A10a and b we obtain

$$SQ(\psi = 0°, g) + SQ(\psi = 90°, g) = 1 \tag{A11}$$

as a normalization condition for any value of g. Furthermore, because of $0 \leqslant g \leqslant 1$, Equation A10b provides

$$0 \leqslant SQ(\psi = 90°, g) \leqslant 1/2 \tag{A12}$$

Equations A11 and A12 can provide a useful method of checking experimentally the measured values of the parallel and perpendicular squareness.

In the case of the iron particles with the packing of 17.1 vol % discussed in the text, the renormalized values of $SQ(\psi = 0°, g)$ and $SQ(\psi = 90°, g)$ were 0.5746 and 0.4254, respectively. Then, the value of g was estimated to be 0.1492, which means that the system investigated here will include a three-dimensional randomness of about 85.1 vol %.