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THE ANISOTROPY OF VERY SMALL COBALT PARTICLES

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Résumé. — Les mesures de l'anisotropie par les méthodes de torsion et de résonance d'un monocristal de l'alliage Cu-2 % Co ont été effectuées à diverses températures pour mesurer l'anisotropie magnétocristalline des grains monodomaines du Co précipité. L'anisotropie à 4.2 °K est indépendante du rayon du grain entre 21 Å et 77 Å. Ceci est en faveur de l'explication de l'anisotropie par un modèle de champs cristallins. La petite variation de l'anisotropie avec la dimension du grain observée à 300 °K peut être liée à une petite variation de l'aimantation à saturation avec la dimension du grain à cette température.

Abstract. — Torque and ferromagnetic resonance measurements on a single crystal of a copper — 2 % cobalt alloy have been made at various temperatures to determine the magnetocrystalline anisotropy of small single domain particles of precipitated cobalt. The anisotropy at 4.2 °K is found to be independent of particle radius from 21 Å to 77 Å, lending support to a crystal field model of the origin of anisotropy. A slight variation of anisotropy with particle size was observed at higher temperatures, and was related to a slight variation in saturation magnetization with particle size at these temperatures.

The magnetocrystalline anisotropy of bulk materials is observed to vary with temperature as a high power of the saturation magnetization — the tenth and twentieth power for iron and nickel respectively [1]. Thus the change in anisotropy of small ferromagnetic particles as a function of their size may reflect in a sensitive fashion the change in saturation magnetization with size. Although there has been some disagreement [2], [3], there is no evidence for an abnormal saturation magnetization in particles of iron [4], [5] or cobalt [6] down to 15 Å radius. Naive use of the results on thin films [7], [8] would imply an effect much larger than that observed on small particles. There remains, however, the problem that a transition must exist between atomic paramagnetism and the coupled behavior of a many atom particle.

Measurement of the anisotropy of small particles may also yield useful information concerning the origin of anisotropy. There are two basically different approaches to this problem within the framework of a Heitler-London approximation to a solid. The first approach (crystal field) [9], [10], [11] assumes the anisotropy to arise because of the electrostatic environment of a magnetic atom without reference to the magnetism of the adjacent atoms. The second approach (anisotropic exchange) [10], [11], [12] emphasizes the fact that the ordinarily isotropic exchange interaction between magnetic atoms may be modified by the presence of spin-orbit coupling of the initially quenched orbital states to become slightly anisotropic. Consider the anisotropy at absolute zero of one atom of cobalt in an electrostatic environment identical to that of cobalt metal but in which its neighbors are non-magnetic. According

to the crystal field picture the anisotropy of this atom is identical to that of the ferromagnetic metal, while in the framework of dominant anisotropic exchange in the ferromagnet, the anisotropy per atom of the single atom case would be much less than in the ferromagnet. We may approach this conceptual experiment by measuring the anisotropy of small particles of cobalt in copper. A spherical particle 20 Å in radius will have approximately 25 % of its atoms on the surface. About one-third of the nearest neighbors of each surface atom are non-magnetic atoms of similar electronic structure and lattice spacing.

The properties of cobalt-rich single domain particles formed by precipitation in copper have been studied in several laboratories [3], [6], [13], [14], [15]. It has recently been demonstrated that the particles in such alloys are initially equiaxed in shape, fcc in structure and coherent with the lattice of the copper matrix and therefore aligned with each other [13], [16], [17]. When these particles are so small that their direction of magnetization can fluctuate thermally [18] they show a magnetic behavior that has been termed "paramagnétique apparente" [19] or superparamagnetic [20].

Experimental techniques. — A single crystal of 2 % cobalt, balance copper, was grown using the Bridgman technique. From this crystal a sample was prepared in the shape of an oblate spheroid with (110) as the major plane. The major axes were 4.3 mm and 1.2 mm.

The cobalt was retained in solution by quenching into an ice-water mixture from 1 000 °C. Precipitate particles of an average radius of 21 Å, 43 Å, and 77 Å were then produced by aging 15, 150 and

2 400 minutes, respectively, at 600 °C. Aging at 580 °C for 7 minutes produced particles averaging 12 Å in radius.

The magnetocrystalline anisotropy is measured by the standard technique shown in Figure 1a. The specimen is rotated in the major principal plane in a uniform magnetic field. The torque is measured with a sensitive torsion balance (1) that can measure torques from 0.06 dyne-cm to 2 000 dyne-cm. The resulting torque shown schematically in figure 1a, can be fitted with a nega-

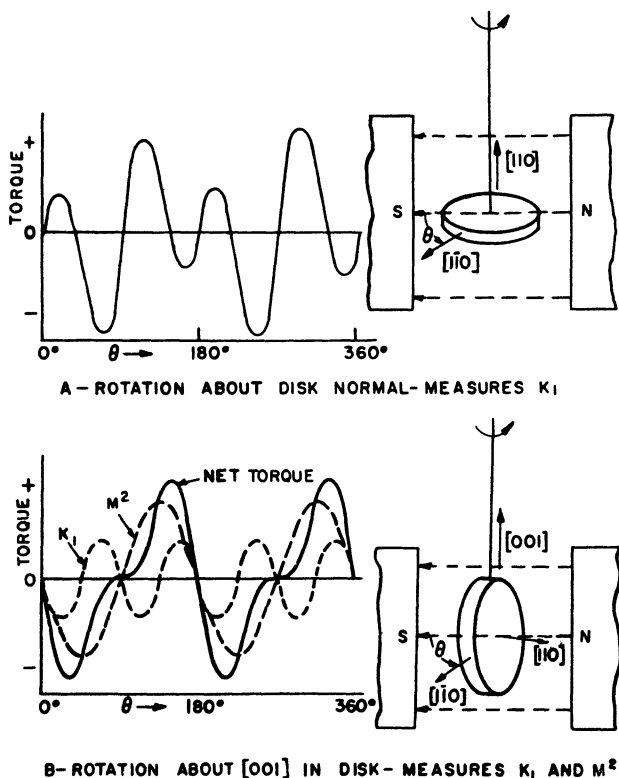


FIG. 1. — The technique employed to determine by mechanical torque measurements the magnetocrystalline anisotropy constant, K_1 and the (magnetization)², M^2 . In A the torque arises from crystal anisotropy alone. In B both crystal and shape anisotropies contribute, are separable, and M^2 may be determined.

tive apparent anisotropy constant K_1 ; a K_2 term is unnecessary. This apparent anisotropy constant is a function of field and temperature (e.g. Fig. 2). At any given temperature and particle size the apparent K_1 is extrapolated against $1/H$ as shown in figure 3. The value obtained by such an extrapolation to infinite field is characterized as the anisotropy constant appropriate to this temperature and particle size. The validity of the $1/H$ extrapolation may be made plausible by consi-

(1) Designed and constructed under the supervision of F. Luborsky of the Instrument Department, General Electric Company, West Lynn, Massachusetts.

deration of two impediments to saturation. The first impediment comes from the thermal fluctuations. A simple theory, to be given elsewhere,

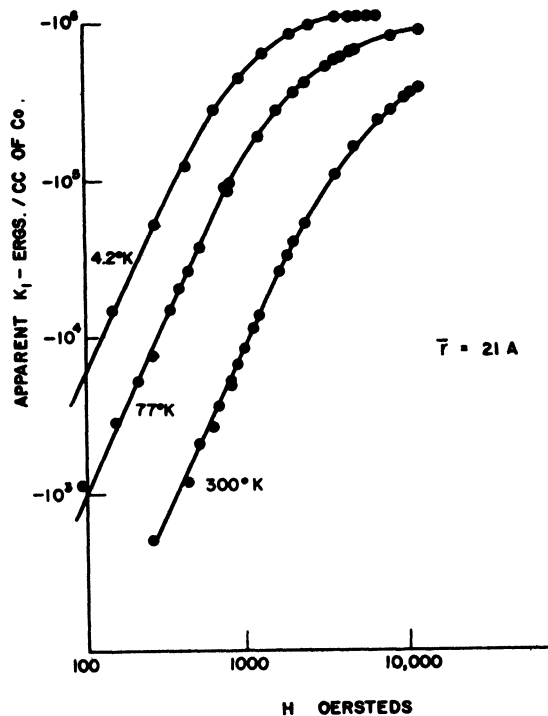


FIG. 2. — Apparent K_1 as determined using Fig. 1-A measurements. The experimental quantity measured directly is K_1 for the sample as a whole. We plot K_1 in terms of the volume of precipitated cobalt.

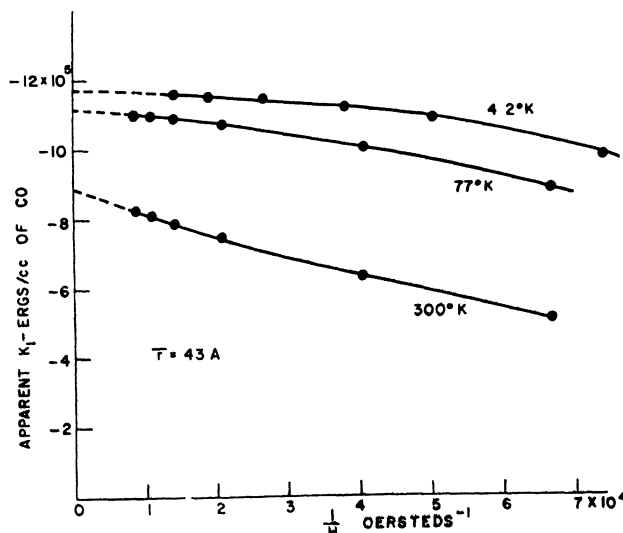


FIG. 3. — The extrapolation to infinite field of the apparent anisotropy constant K_1 .

shows that $K(H)/K(\infty) = (I(H)/I(\infty))^{10}$ for this effect, in the approximation that $Kv/kT \ll 1$ where v is the volume of the particle. In the same approximation the magnetization approaches satu-

ration by a linear extrapolation against reciprocal field [2], [4], [19], [21]. Another possible impediment is the fact that the particles may have other than cubic anisotropy — for instance, a shape or surface anisotropy [22]. It has been shown [23], [24] that uniaxial anisotropies in cubic array give an apparent cubic anisotropy that vanishes in large fields as $1/H$.

Magnetization measurements are made by rotating the specimen about the [001] direction in the major principal plane of the spheroid. The shape anisotropy gives a term in the torque proportional to the square of the magnetization (M^2) at a given field, and at least in the limit of very high and low magnetizations is given by $L_I = -(V\Delta NM^2(H) \sin 2\theta)/2$, where θ is the angle between the field and the [110] axis as shown in figure 1*b*, V is the volume of the sample and ΔN is the difference between the demagnetizing factors along the major and minor axes. ΔN is 6.4 for our specimen. The crystal anisotropy gives a term $L_K = -(VK_1 \sin 4\theta)/2$. Consequently, the magnetization may be derived by a simple decomposition of the experimental curve as indicated schematically in figure 1*b*. The torque due to magnetization may be extrapolated against $1/H$ to obtain the saturation magnetization. At low fields, for superparamagnetic particles, the $\sin 2\theta$ term is proportional to the square of the field, thus indicating the constant initial susceptibility associated with superparamagnetism. This initial susceptibility was used to determine the average particle size [4], [6].

Ferromagnetic resonance measurements were made on the same samples at various temperatures employing standard techniques at 9.2 G Hz.

Results and discussion. — Figure 4 plots the primary results of this experiment. (For the 21 Å particles at 300 °K and for the 12 Å particles even at 4.2 °K, the $1/H$ extrapolation required was so extreme that an accurate value of anisotropy could not be established, although for the latter the value was apparently between 1.0 and 1.4×10^6 ergs/cc of Co.) The anisotropy at 4.2 °K is seen to be independent of particle size within the accuracy of measurement. A dashed line is drawn to indicate the results to be expected if the surface atoms were assumed to have an anisotropy equal to 90 % of that of the interior atoms. Thus we infer that the anisotropy of the surface atoms is identical (within 10 %) to that of the volume atoms. This supports the crystal field origin of the anisotropy. As pointed out by Van Vleck and emphasized by Yosida and Tachiichi, there are certain theoretical difficulties with this picture. The experimental result, however, should encourage reexamination of this problem.

At higher temperatures there is a small but noti-

ceable decrease in the extrapolated anisotropy as the particle size is made smaller. The anisotropy at 300 °K extrapolated to infinite particle size is

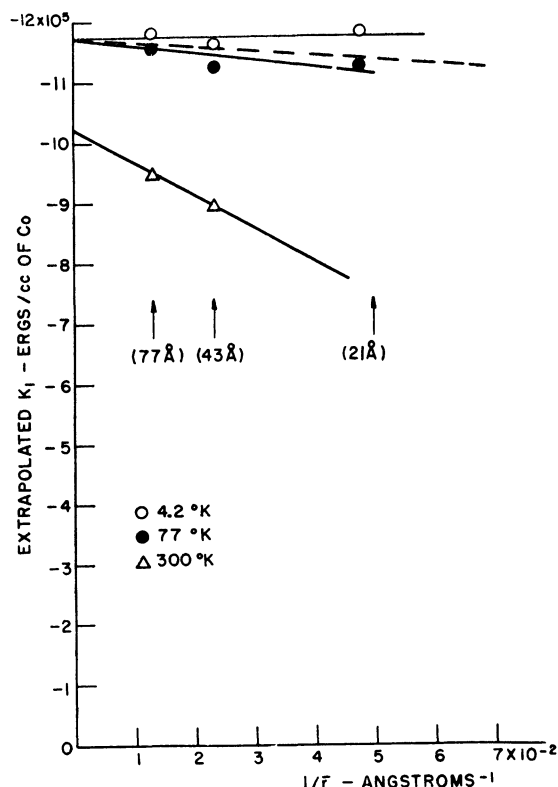


FIG. 4. — Dependence of the extrapolated anisotropy constant K_1 upon particle size for the indicated temperatures. The dotted line shows the dependence expected if the surface atoms have 90 % of the crystal anisotropy of volume atoms.

seen to be about 13 % less than its value at 4.2 °K. Bulk hexagonal cobalt is variously reported [25], [26], [27] to change its saturation magnetization 1.3 % to 1.7 % in the temperature interval 0 °K to 293 °K. Since the temperature dependence of the saturation magnetization of face-centered cobalt is expected to be close to that of the hexagonal phase [28], the change in anisotropy with temperature is in fair accord with a tenth power dependence of anisotropy upon saturation magnetization. Extension of these arguments to the change of anisotropy with particle size would suggest that 43 Å cobalt particles at 300 °K have a saturation magnetization only 1 %-2 % less than that of the bulk material at the same temperature. If this inference be correct, this result places much closer limits upon the striking independence of saturation with particle size found earlier [6].

Direct measurements of the saturation magnetization at 4.2 °K gave identical results (± 2 %) for

the samples with average radii 21 Å, 43 Å and 77 Å.

Table 1 shows a comparison of the results found by torque and resonance measurements. The

TABLE I

COMPARISON OF MECHANICAL TORQUE AND FERROMAGNETIC RESONANCE OBSERVATIONS ON THE SAME SPECIMEN

TEMP. °K	MECHANICAL TORQUE			FERROMAGNETIC RESONANCE		
	$-\left(\frac{K_1}{M_S}\right)_\infty$ ± 17 Oe	$-\left(\frac{K_1}{M_S}\right)_{3kOe}$ ± 17 Oe	$-\frac{K_2}{M_S}$ Oe	$-\frac{K_1}{M_S}$ ± 25 Oe	$-\frac{K_2}{M_S}$ ± 25 Oe	g ± .03
			$\bar{r} = 77 \text{ \AA}$			
300	678	668	—	725	60	2.07
77	833	805	—	845	170	2.05
4.2	846	813	—	850	200	2.05
			$\bar{r} = 21 \text{ \AA}$			
300	—	56	—	60	— 7.2	2.09
77	800	360	—	610	31	2.05
4.2	842	730	90 ± 90	—	—	—

values for K_2 reported reflect the relative sensitivity of resonance measurements to higher order terms. At 4.2 °K the results are identical. This shows that the torque measurements, which measure an average, are not weighted by a small portion of material with very large anisotropy. The lack of coincidence of the apparent anisotropies at higher temperatures is not unexpected but cannot be discussed here due to space limitations.

Conclusions. — 1. The cubic magnetocrystalline anisotropy of the face-centered cobalt-rich precipitate in the alloy 2 % cobalt-copper is $-1.17 \pm .02 \times 10^6$ ergs/cc of Co at 4.2 °K and is independent of the particle radius from 21 Å to 77 Å.

2. These data suggest that the origin of magnetocrystalline anisotropy is to be found in the influence of the electrostatic environment of the cobalt atom rather than in anisotropic exchange interaction.

3. Saturation magnetization measurements of the alloy at 4.2 °K are identical (± 2 %) for particles of 21 Å, 43 Å and 77 Å in radius.

4. From the change of anisotropy with particle size at room temperature, it is inferred that at 300 °K the saturation magnetization of 43 Å particles is 1 %-2 % less than that of the bulk material.

5. Torque and resonance measurements of the anisotropy give identical results at low temperatures but deviate slightly from one another at elevated temperatures.

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12, 30, Professor Knappwost has informed us privately that his views have undergone some revision since this publication.

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DISCUSSION

M. Weil. — Êtes-vous absolument sûr qu'il n'y a aucune autre origine à l'anisotropie ?

Mr. Jacobs. — The existence of this cubic anisotropy term, measured in two different ways, seems very difficult to explain by any other kind of anisotropy ; i.e. other than the magnetocrystalline kind. Your own experiments indicate that the precipitate has the f.c.c. structure. From

the theoretical side, however, there may be alternative approaches to those enumerated.

Mr. Zylstra. — When you assume an anisotropic exchange, should one not expect to get an influence on the Curie temperature when magnetizing in the [100] or the [111] direction ?

Mr. Jacobs. — I don't know whether there should be such an effect. The experiments here were all carried out at a relatively small value of the temperature ratio T/θ_c .