The Additional Magnetic Anisotropy Induced by Magnetic Anneal in Ferromagnetic Face-Centered Cubic Solid Solutions : Part I. Dependence of the Induced Magnetic Anisotropy on the Temperature and Duration of Magnetic Anneal, on the Measuring Temperature, and on the Alloy Composition in Face-Centered Cubic Nickel-Cobalt Alloys

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The Additional Magnetic Anisotropy Induced by Magnetic Anneal in Ferromagnetic Face-Centered Cubic Solid Solutions*

Part I. Dependence of the Induced Magnetic Anisotropy on the Temperature and Duration of Magnetic Anneal, on the Measuring Temperature, and on the Alloy Composition in Face-Centered Cubic Nickel-Cobalt Alloys.

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Synopsis

We have studied systematically the character of the induced magnetic anisotropy in face-centered cubic Ni-Co alloys, using a torque magnetometer designed specially for high-temperature measurements. Specimens used are polycrystalline disks of 10.57, 20.78, 30.84, 40.67, 50.17, and 60.20 %Co-Ni alloys and $(1\bar{1}0)$ disk single crystal of 12 %Co-Ni alloy. The results and conclusions obtained are as follows : — The magnetic anisotropy energy, E_u, induced by magnetic anneal is uniaxial. Generally, as the duration of magnetic anneal increases, E_u increases nearly exponentially and, as the temperature of magnetic anneal becomes higher, the rate of development of E_u increases but its saturation value decreases. The development of E_u can not be described in terms of single relaxation time and the associated relaxation times become longer as the duration of magnetic anneal increases. The dependence of E_u, on the temperature, Θ, of magnetic anneal and on the measuring temperature, T, can be expressed well by an expression E_u=const. $\times\{(I_\Theta/I_0)^2/\Theta\}(I_T/I_0)^2$, where I_Θ, I_T, and I_0 are the values of saturation magnetization at Θ(°K), T(°K), and 0°K, respectively, which was derived by Taniguchi and Yamamoto from the so-called directional order theory. The comparison of the measured data on the alloy composition dependence of E_u as corrected for the composition dependence of the Curie temperature with Néel's theoretical formula indicates that the ordering energy of Ni-Co alloys is negative and hence the alloys may be of the precipitation type.

In connection with this study, the temperature dependence of the cubic magnetocrystalline anisotropy constants, K_1 and K_2, was measured with 12 %Co-Ni alloy and pure nickel, and it has been found that, as the temperature rises, K_1 of 12 %Co-Ni alloy changes from positive to negative at about 150°C, while K_1 of nickel takes small positive values above 200°C and that K_2 of 12% Co-Ni alloy is always positive, while K_2 of nickel changes from positive to negative at about 100°C.

I. Introduction

When a ferromagnetic cubic solid solution crystal is heat-treated in an externally applied magnetic field, a magnetic anisotropy is induced additionally, of which the direction of easy magnetization is nearly parallel to the annealing field. Because of this induced magnetic anisotropy, the magnetization curve changes

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its shape by magnetic annealing or magnetic field cooling; it is very steep when measured along the direction parallel to the annealing field, while it is very flat in the perpendicular direction. Attention was first called to this magnetic annealing effect, when it was studied by Kelsall[(1)] on some nickel-iron alloys in 1934, although the effect was first discovered by Pender and Jones[(2)] in 1913 with 3.5% Si-Fe alloy. Since then, numerous investigators have studied experimentally this phenomenon with various alloys,[(3)] but most of the studies concerned only with the change in shape of the magnetization curve due to cooling in an applied magnetic field. Thus, we hardly knew about the nature of this induced magnetic anisotropy until Chikazumi and Oomura[(4)] recently measured directly the induced magnetic anisotropy energy on nickel-iron alloys and found that its magnitude increased monotonously with increasing iron content.

Bozorth *et al.*[(5)] proposed first, in connection with his measurements on iron-nickel-cobalt alloys, that the induced magnetic anisotropy might be due to the "plastic deformation caused by magnetostriction" at high temperatures. Although some objections had already been made to this proposal, it may be most fatal that the magnetic anisotropy is induced even in an alloy of zero magnetostriction. Chikazumi[(6)] proposed the "strain-in-directional-order" theory in order to explain the order of magnitude of the induced magnetic anisotropy in nickel-iron alloys nearby Ni_3Fe, the disappearence of the induced anisotropy at perfect order, etc. These facts can be explained as well in terms of the "elongated order phase" proposed by Iida,[(7)] which is similar to the "elongated precipitate phase" in some permanent magnet alloys. Although the physical origins of the induced anisotropy supposed in these two interpretations are quite different from each other, the former relating to the magnetostriction while the latter to the difference in saturation magnetization between order and disorder phases, both interpretations are based on the same phenomenon of ordering. Thus, the above-mentioned experimental results obtained by Chikazumi and Oomura[(4)] on the composition dependence of the induced magnetic anisotropy can not be explained by any of these interpretations.

Recently, a more general theory was presented by Taniguchi and Yamamoto[(8)] and, independently, by Néel.[(9)] This so-called "directional order" theory is based on the presence of anisotropic magnetic coupling between atoms in ferromagnetic cubic solid solutions, so that the magnetic anisotropy can be induced by magnetic

(1) G. A. Kelsall: Physics, 5(1934), 169.
(2) H. Pender and R. L. Jones: Phys. Rev., **1** (1913), 259.
(3) See C.D. Graham, Jr., Magnetic Annealing, in *Magnetic Properties of Metals and Alloys*, ASM(1959), p. 288.
(4) S. Chikazumi and T. Oomura: J. Phys. Soc. Japan, **10** (1955), 842.
(5) J.E. Dillinger and R.M. Bozorth: Physics, **6** (1935), 279. R.M. Bozorth and J.E. Dillinger: Physics, **6** (1935), 285.
(6) S. Chikazumi: J. Phys. Soc. Japan, **5** (1950), 327, 333.
(7) S. Iida: cited by S. Kaya: Rev. Mod. Phys., **25** (1953), 49.
(8) S. Taniguchi and M. Yamamoto: Sci. Rep. RITU, **6** (1954), 330. S. Taniguchi: Sci. Rep. RITU, **7** (1955), 269.
(9) L. Néel: Compt. rend., **237** (1953), 1613; J. de phys. rad., **15** (1954), 225.

anneal even in a solid solution which is ideal in the sence of the statistical theory of the mixtures. Chikazumi[4] himself had reached to the conclusion that his experimental results on the composition dependence of the induced magnetic anisotropy should be interpreted by the same idea. Later, however, he[10] made a detailed study on the orientational dependence of the induced magentic anisotropy using a Ni_3Fe single crystal and found a rather pronounced disagreement with the directional order theory.

The above-mentioned Chikazumi's[4,10] recent studies on nickel-iron alloys are worthy as a pioneer work for elucidating the nature of the induced magnetic anisotropy by direct measurements, but the presence of superlattice Ni_3Fe in this alloy system may complicate the situation and thus may lead to an erroneous conclusion. So, we have studied systematically the induced magnetic anisotropy with the face-centered cubic nickel-cobalt alloy system, which seems to be one of the most ideal solid solutions among ferromagnetic alloys. We have at first measured the induced magnetic anisotropy as a function of the temperature and duration of magnetic anneal, temperature of measurement, and alloy composition, of which the results are reported in this paper (Part I). Further, we have studied the orientational dependence of the induced magnetic anisotropy with nickel-cobalt single crystals, and also with face-centered cubic nickel-iron single crystals, in order to see if the above-mentioned disagreement between the theory and experiment found by Chikazumi[10] on Ni_3Fe single crystal might be due to the general character of nickel-iron alloys or not, of which the results are reported in Part II of this paper by Aoyagi.[11]

II. Experimental apparatus and specimens

(1) Experimental apparatus

The measurement of magnetic anisotropy was made using a specially designed torque magnetometer, which is shown diagrammatically in Fig. 1. The disc specimen *Sp* placed between two small quartz discs constituting the lower end of a quartz rod *R* is suspended by a phosphor bronze wire *P* from the head *H*, which is provided with an adjuster of the vertical position of the suspended system. A jewel bearing system B_1 is used to avoid a horizontal displacement of the disc specimen. The upper part of the apparatus, separated from the lower part by a Wilson seal and a thrust bearing B_2, can rotate about its vertical axis together with the suspended system. The orientation of the specimen disc is observed by a mirror M_1, attached to the suspended system, and the torque exerted on the specimen disc is determined by the torsion angle of the phosphor bronze wire *P*, which is given by the angle between orientations of two mirrors M_1 and M_2, the latter being attached to the rotatable upper part of the apparatus. Both mirrors are adjusted to be paralle when no torque is exerted on the specimen disc. Orientations of the mirrors are measured by means of a autocollimated telescope

(10) S. Chikazumi: J. Phys. Soc. Japan, **11** (1956), 551.
(11) K. Aoyagi: Sci. Rep. RITU, **A13** (1961), 137.

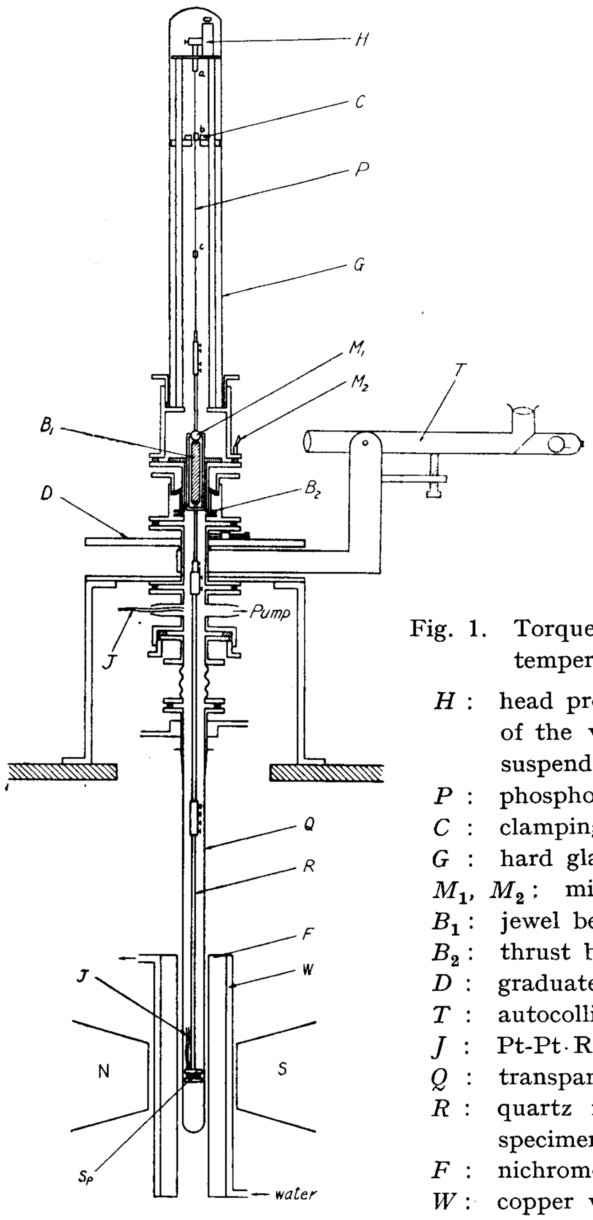

Fig. 1. Torque magnetometer for high-temperature measurements.

- H : head provided with an adjuster of the vertical position of the suspended system.
- P : phosphor-bronze suspension wire,
- C : clamping grip,
- G : hard glass tube,
- M_1, M_2 : mirrors,
- B_1 : jewel bearing system,
- B_2 : thrust bearing,
- D : graduated disc,
- T : autocollimated telescope,
- J : Pt-Pt·Rh thermocouple,
- Q : transparent quartz tube,
- R : quartz rod for supporting the specimen disc,
- F : nichrome furnace,
- W : copper water-jacket,
- Sp : specimen disc,
- N, S : pole-pieces of an electromagnet.

T, which is rotatable around a graduated disc D.

For the high temperature measurements and for the heat treatment of the disc specimen in magnetic field, a small nichrome furnace F, provided with a copper water-jacket W, is placed between pole-pieces of an electromagnet N-S. To prevent the specimen from oxydation at high temperatures, the suspended system is enclosed in an evacuated vessel which consists of hard glass tube G, a brass chamber, a transparent quartz tube Q, etc. connected together by rubber seals. A Pt–Pt·Rh thermocouple J is introduced for the temperature measurement.

The torsion constant of the phosphor bronze suspension wire P can be altered by changing the clamping position from a to b or to c by means of a grip C, which is movable vertically along the wire and can clamp the wire by outside operation without injuring vacuum. This clamping grip C is also used to fix the orientation of the specimen disc relative to the direction of magnetic field applied during annealing. Values of the torsion constant of the suspension wire P, determined from the measurement of the oscilation period of the suspended system using Maxwell's rod as the moment of inertia, are 32.6, 73.4 and 195 dyne·cm/degree for the clamping positions a, b and c, respectively.

(2) *Specimens*

(a) Polycrystalline specimens

Nickel and cobalt, both of electrolytic quality, were melted together in a vacuum high-frequency induction furnace and the melts were cast in vacuum. The ingots thus mades were hot-forged and then cold-rolled to sheets of about 1 mm thickness. Discs of about 15 mm diameter were cut out from the sheets by lather-maching and their thickness was further reduced to about 0.5 mm by polishing with Emery papers. Polycrystalline specimen discs of 10, 20, 30, 40, 50, and 60 %Co-Ni alloys (in balanced composition), thus prepared, were then annealed at 1000°C for an hour in vacuum in order to remove internal stress due to cold working. The results of chemical analysis and the dimensions of the speciemen discs are given in Table 1.

Table 1. Compositions, dimensions, and saturation magnetic fields of disc specimens of nickel-cobalt polycrystals.

Specimen mark	Composition (wt.-% Co)	Dimensions		Saturation field (Oe)
		Diameter(mm)	Thickness(mm)	
10 %Co	10.57	15.20	0.463	200
20 %Co	20.78	15.20	0.479	220
30 %Co	30.84	15.20	0.491	260
40 %Co	40.67	16.00	0.451	280
50 %Co	50.17	16.00	0.464	310
60 %Co	60.20	16.00	0.453	330

(b) Single crystal specimens

A single crystal of 12 %Co-Ni alloy, about 20 mm in diameter and 25 mm in length, was grown from the melt of the mixture of nickel and cobalt, all of electrolytic quality, by lowering the crusible containing the melt slowly at the rate of about 1–4 cm/hour in an evacuated carbon-tube furnace. The ingot thus made was pre-etched with conc. HNO_3 in order to examine the state of crystallization. The single crystal was orientated using the light-figure method[12] after etched with boiling saturated aqueous solution of ferric chloride for 1–2 minutes and then a plate, of which the plate surface is parallel to a $(1\bar{1}0)$ plane and the thickness is about 0.5 mm, was cut out of it by a jewler's saw. The shaping of the single crystal plate into a thin disc was performed by repeating grind on Emery papers and etch in conc. HNO_3 containing a small amount of ferric chloride. Since, in the de-

(12) M. Yamamoto: Sci. Rep. Tôhoku Univ., **31** (1943), 121. M. Yamamoto and J. Watanabé: Sci. Rep. RITU, **A7** (1955), 173; **A9** (1957), 295.

termination of the magnetic anisotropy constant by the torque magnetometer method, a serious error may be introduced by the fluctuation in diameter of the disc specimen, the single crystal disc was carefully polished so as to be less than 0.5% in diameter fluctuation which corresponds to less than about 40 erg/cm^3 in anisotropy constant for the specimen used. Finally, it was electrolytically polished and annealed at 1000°C for 1 hour in vacuo. The single crystal disc thus prepared is 9.787 mm in diameter and 0.432 mm in thickness. Its crystal orientation was subsequently checked by means of back-Laue X-ray photograph, which indicated that the inclination of its plate surface from a $(1\bar{1}0)$ plane was within 3° and the fluctuation of crystal orientation within the specimen was within 2°. These deviations never give a serious error in the determination of the anisotropy constant, as may be seen from a simple calculation. The composition of the single crystal disc was determined to be 12 %Co by X-ray fluorescence analysis of the specimen itself. It is to be noted that the comparison of the observed value of the first cubic ferromagnetic anisotropy constant, K_1, with those determined previously[(13)] gives the value of 15 %Co.

III. Experimental results

(1) Dependence of the induced ferromagnetic anisotropy on the temperature and duration of magnetic anneal.

A polycrystalline disc of 30.84 %Co–Ni alloy was employed to measure the dependence of the induced magnetic anisotropy on the temperature and duration of magnetic anneal. Firstly, the magnetic torque (L) curve was measured, using magnetic field of 1050 Oe, which was strong enough to saturate the specimen disc (cf. Table 1), on the specimen disc in the state cooled rapidly from above the Curie temperature (about 700°C) to room temperature in the absence of an applied magnetic field, namely in the state not affected by magnetic anneal. Secondly, the specimen disc was heated, without magnetic field, at about 750°C for 30 minutes and then cooled in the furnace down to a temperature, Θ. After held at Θ for 6 minutes, it was subjected to magnetic field of 1700 Oe applied parallel to its plate surface for a time interval, t, and then it was cooled rapidly in the presence of the same applied magnetic field to room temperature, where the torque measurement was carried out. This procedure was repeated for various values of the temperature, Θ, and duration, t, of magnetic anneal.

The curve (1) in Fig. 2 is the toruqe curve measured in the state cooled rapidly from above the Curie temperature in the absence of an applied magnetic field, and the curve (2) is referred to the state annealed at 400°C for 30 hours, specially, in the presence of an applied magnetic field of 2150 Oe. It was confirmed that the curve (1) was not influenced by the cooling rate, and thus it may be due to the magnetorcrystalline anisotropy which is originated from the deviation of the orientation distribution of crystal grains from the isotropic one. Then, we can

(13) M. Yamamoto: Sci. Rep. RITU, **A4** (1952), 14, and literature cited in it.

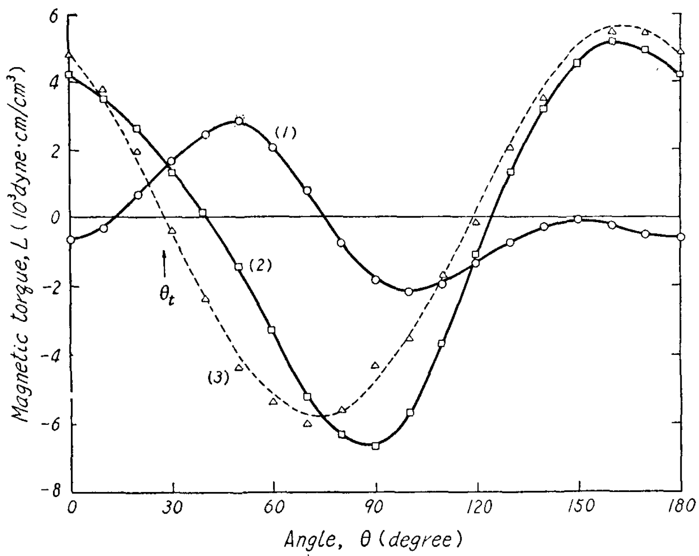

Fig. 2. Magnetic torque (L) curves in variously heat-treated states of a polycrystalline disc of 30.84 %Co-Ni alloy.

curve (1) : cooled from above the Curie temperature in the absence of an applied magnetic field,
curve (2) : annealed at 400°C for 30 hours in the presence of magnetic field of about 2150 Oe applied along the direction, θ_t, in the disc surface,
triangles : (2)-(1),
curve (3) : calculated from $L=-K_u\sin 2\,(\theta-\theta_0)$, where $\theta_0=\theta_t$.

obtain the torque due solely to an additional magnetic anisotropy induced by magnetic anneal by subtracting the curve (1) from the curve (2). Thus determined torque values are shown by open triangles in Fig. 2. While, the dashed curve (3) is a calculated torque curve of

$$L=-K_u \sin 2\,(\theta-\theta_0)\ , \tag{1}$$

which is obtained from the formula of the uniaxial ferromagnetic anisotropy energy

$$E_u=-K_u \cos^2(\theta-\theta_0) \tag{2}$$

through a relation $L=-\partial E_u/\partial\theta$, where K_u is the constant of the uniaxial anisotropy energy and θ_0 is its direction of easy magnetization, which is taken to be the direction, θ_t, of magnetic field applied during annealing. It may be seen from the figure that the measured points (open triangles) lie well on the calculated curve (3). Thus, we can say that the magentic anisotropy induced additionally by magnetic anneal is uniaxial and its direction of easy magnetization is parallel to that of magnetic field applied during annealing.

Fig. 3 shows the torque curves due solely to the uniaxial magentic anisotropy induced by magnetic annealing at 450°C for various time intervals, t, in an externally applied field of 1700 Oe. Here, it is to be noticed that a small but finite uniaxial magnetic anisotropy is induced even for $t=0$. This may be considered as induced during rapid cooling (for 2–3 minutes) from the magnetic annealing temperature, Θ, to room temperature. Then, it may be larger as Θ is higher, since

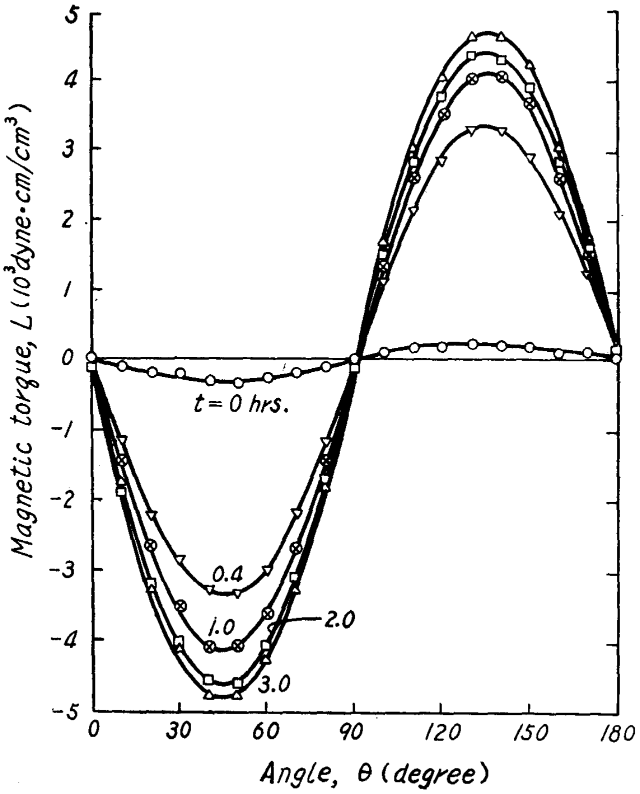

Fig. 3. Magnetic torque curves of a polycrystalline disc of 30.84 % Co-Ni alloy, as dependent on the duration, t, of magnetic anneal at 450°C.

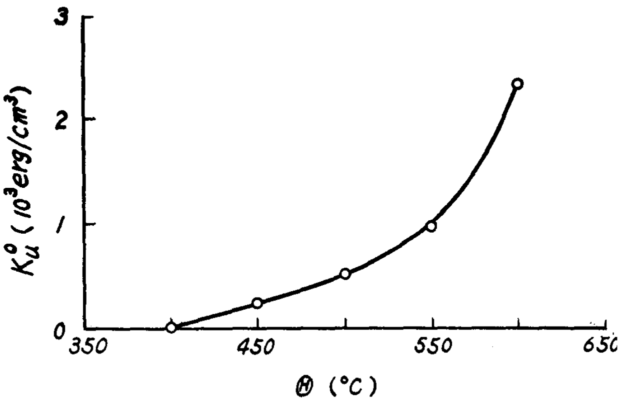

Fig. 4. Constant of the uniaxial magnetic anisotropy, K_u°, induced during cooling from the magnetic annealing temperature, Θ, to room temperature, as dependent on Θ in a polycrystalline disc of a 30.84 % Co-Ni alloy.

the time required for cooling the specimen disc from Θ to room temperature becomes longer. In fact, its anisotropy constant, K_u°, varies with Θ in such a way as shown in Fig. 4. Thus, since $K_u^\circ(\Theta)$ may be considered as independent of the duration, t, of magnetic anneal, it should be subtracted from the measured values of $K_u(\Theta, t)$. The resulting $K_u(\Theta, t)$ values are plotted against t for various Θ values in Fig. 5, which shows that, as the duration, t, of magnetic anneal increases, the induced uniaxial magentic anisotropy increases rapidly at first and then more and more slowly, finally attaining to saturation and that, as the temperature, Θ, of magnetic anneal rises, the rate of development of the induced anisotropy increases while its saturation value decreases. $K_u(\Theta, t=\infty)$, namely, the saturation

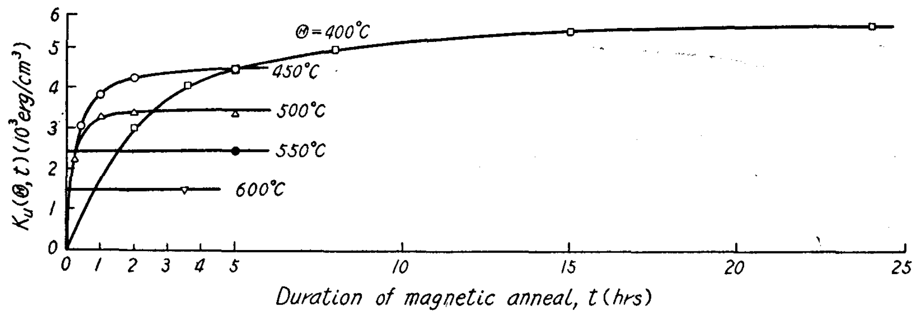

Fig. 5. Uniaxial anisotropy constant, $K_u(\Theta, t)$, as dependent on the duration, t, of magnetic anneal at various temperatures, Θ, in a polycrystalline disc of 30.84 %Co-Ni alloy.

value of $K_u(\Theta, t)$, as determined from Fig. 5, is dependent on Θ in such a way as shown in Fig. 6.

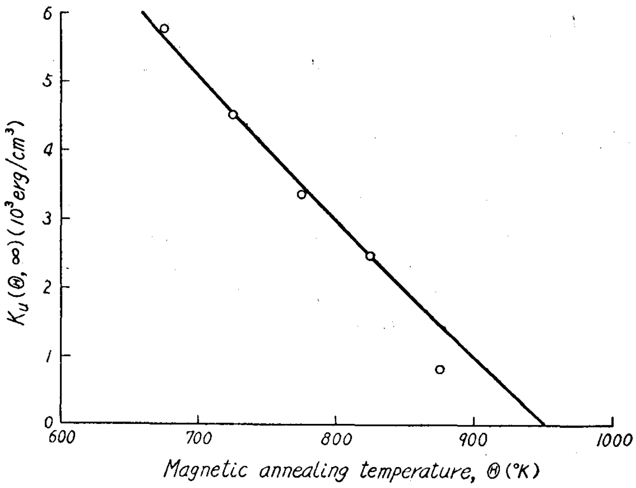

Fig. 6. Saturation value of the uniaxial anistoropy constant, K_u (Θ, ∞), as dependent on the temperature, Θ, of magnetic anneal in a polycrystalline disc of 30.84 %Co-Ni alloy. Circles : measured values, solid line : $(I_\Theta/I_0)^2/\Theta$ vs. Θ curve.

In order to see if the measured data obtained above might be influenced by the time interval, t_p, during which the specimen was kept at an annealing temperature, Θ, before the annealing magnetic field was applied, $K_u(\Theta=450°C, t)$ was measured for t_p=6 minutes, 1 hour, and 3.5 hours. The results obtained are as shown in Fig. 7, from which we see that the saturation K_u value, K_u $(\Theta, t=\infty)$, is hardly influenced while the rate of the development of the induced magentic anisotropy is changed considerably by t_p. A more instructive view is obtained when in $[\{K_u(\Theta, t=\infty)-K_u(\Theta, t)\}/K_u(\Theta, t=\infty)]$ is plotted against t by taking Θ and t_p as parameters. It may be seen from Figs. 8 and 9 that the development of the induced magnetic anisotropy can not be described in terms of a single relaxation time, the relaxation time increasing with increasing duration, t, of magnetic anneal. It is to be noted that the increase in t_p apparently results the disappearence of shorter parts of the relaxation times (cf. Fig. 9).

(2) *Dependence of the induced uniaxial magnetic anisotropy on the measuring temperature, and the temperature dependence of the cubic ferromagnetic anisotropy constants, in 12 %Co-Ni alloy and nickel.*

The $(1\bar{1}0)$ disc of 12 %Co-Ni single crystal was used to study the dependence of the induced uniaxial magetic anisotropy on the measuring temperature. The

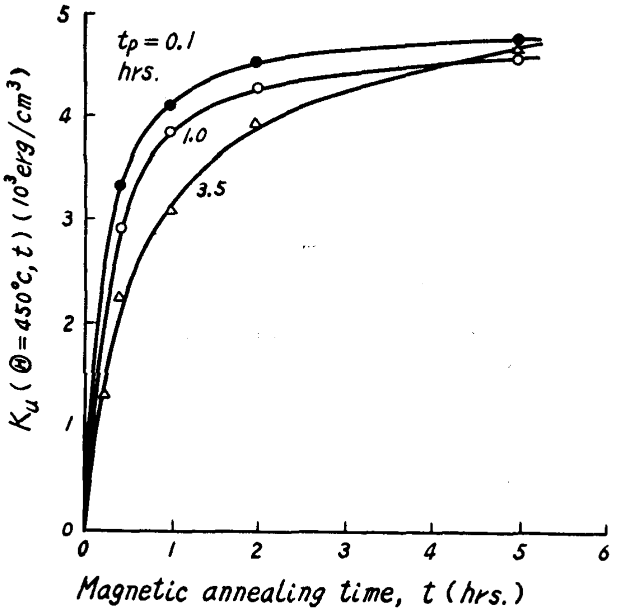

Fig. 7. Constant of uniaxial ferromagnetic anisotropy induced by magnetic annealing at 450°C, $K_u(\Theta=450°, t)$, after held at various time intervals, t_p, at that temperature, as dependent on the duration, t, of magnetic anneal in a polycrystalline disc of 30.84 %Co-Ni alloy.

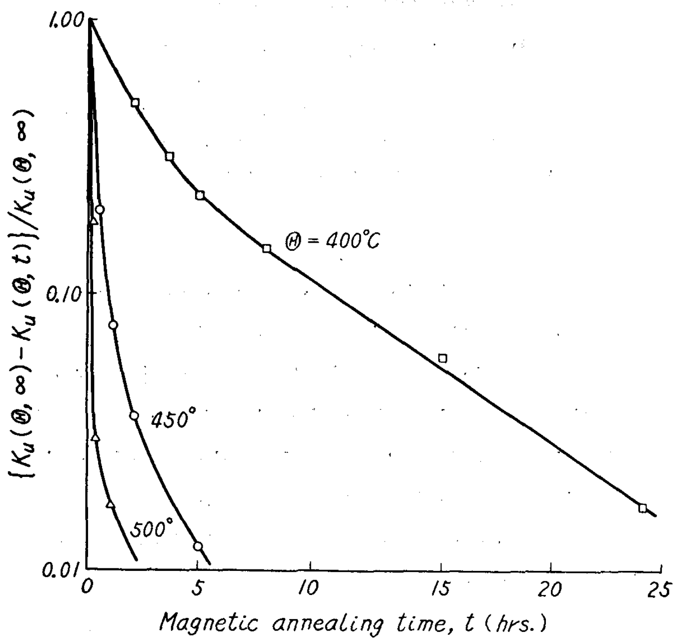

Fig. 8. ln $[\{K_u(\Theta, \infty)-K_u(\Theta, t)\}/K_u(\Theta, \infty)]$ as dependent on the duration, t, of magnetic annealing at Θ=400, 450, and 500°C in a polycrystalline disc of 30.84 %Co-Ni alloy.

reason why not a polycrystalline specimen but the single crystal specimen was employed is to determine annexedly the temperature dependence of the cubic ferromagnetic anisotropy constants, K_1 and K_2. According to our studies,(13,14) at room temperature, K_1, which is negative for pure nickel, becomes positive with an addition of cobalt by only 4%, but it again becomes negative beyond about 19% Co. Such a complicated variation of K_1 with composition is curious in view of the fact that face-centered cubic nickel-cobalt alloys constitute a very simple solid solution system, and we may expect any information for this from the temperature dependence of K_1.

The specimen disc was annealed at 450°C for 5 hours with the presence of an applied field of about 1700 Oe applied along a direction 40° apart from the [001] direction in the $(1\bar{1}0)$ plate surface of disc. This annealing time is sufficient to saturate the development of the induced magnetic anisotropy at 450°C, as may be seen from Fig. 5. Magnetic torque curves were measured from room temperature to 500°C, just below the Curie temperature, successively with an about 50°C step. Values of K_u, K_1, and K_2 for each

(14) M. Yamamoto and S. Taniguchi: Nippon Kinzoku Gakkai-shi, **25** (1961), 225, 229 (in Japanese).

measuring temperature, T, were obtained from Fourier analysis of the measured torque curves, since, for 12 %Co-Ni alloy, K_u is smaller than K_1 and both decrease in manners different from each other with increasing temperature, so that the values of K_u, K_1, and K_2 can not be determined accurately by subtracting the torque curve for the state annealed without magnetic field from that for the magnetically annealed state.

It has been found that the measured torque curves can be described completely in terms of K_u, K_1 and K_2. As an example, Fig. 10 shows the values of the magnetic torque, L, measured at room temperature (open circules), the component torque curves, L_c and L_u, which are, respectively, due to the cubic and uniaxial magnetic anisotropies, and the composite torque curve, L_t, which is drawn using the values $K_u = 1.59 \times 10^3$ erg/cm^3, $\theta_0 = 42.8°$, $K_1 = 6.8 \times 10^3$ erg/cm^3,

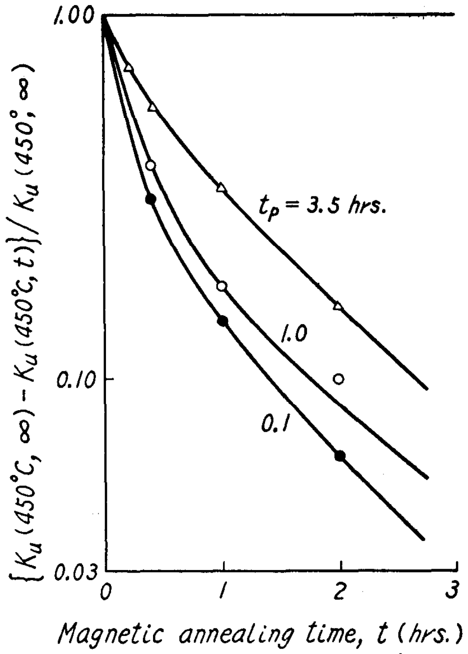

Fig. 9. In [{K_u(450°C, ∞) − K_u(450°C, t)}/K_u (450°C, ∞)] as dependent on the duration, t, of magnetic annealing at 450°C after kept at the same temperature for various time intervals, t_p, in a polycrystalline disc of 30.84 %Co-Ni alloy.

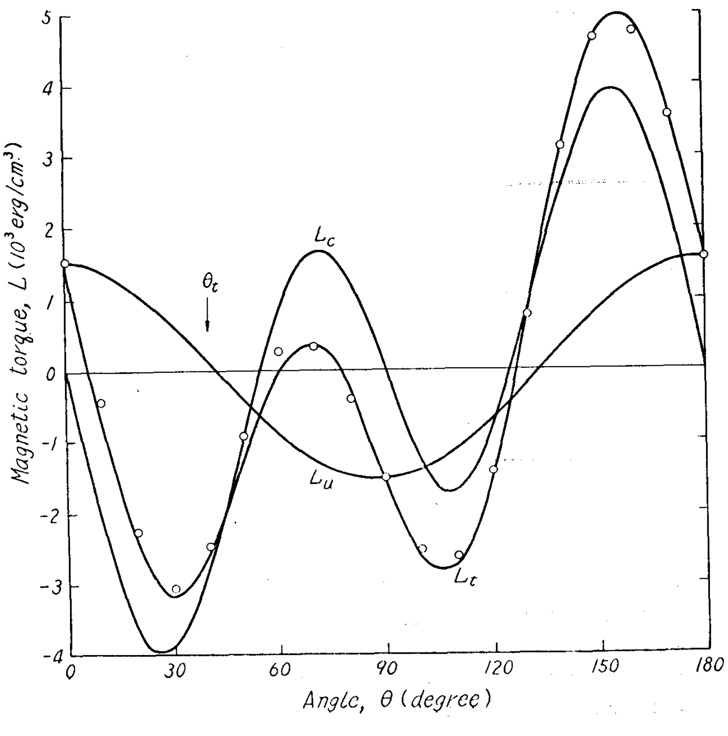

Fig. 10. Measured magnetic torque data (open circles), Fourier-analysed component torque curves (L_c and L_u), and the composite torque curve (L_t) at room temperature of a (1$\bar{1}$0) disc of 12% Co-Ni single crystal annealed at 450°C for 5 hours in magnetic field of about 1700 Oe applied along a direction 40° apart from the [001] direction in the plate surface.

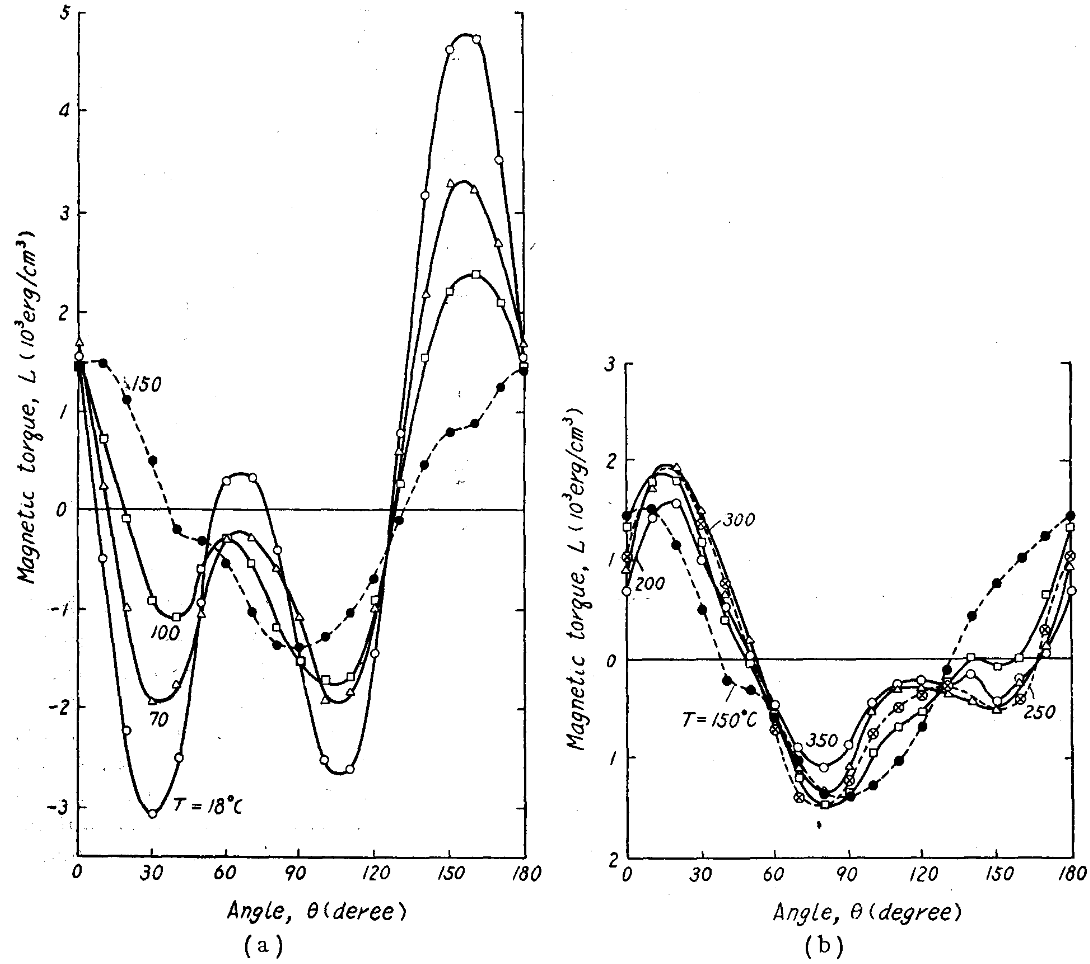

Fig. 11. Magnetic torque curves measured at various high temperatures of a (1$\bar{1}$0) disc of 12 %Co-Ni single crystal annealed at 450°C for 5 hours in magnetic field of about 1700 Oe applied along a direction 40° apart from the [001] direction in the plate surface.

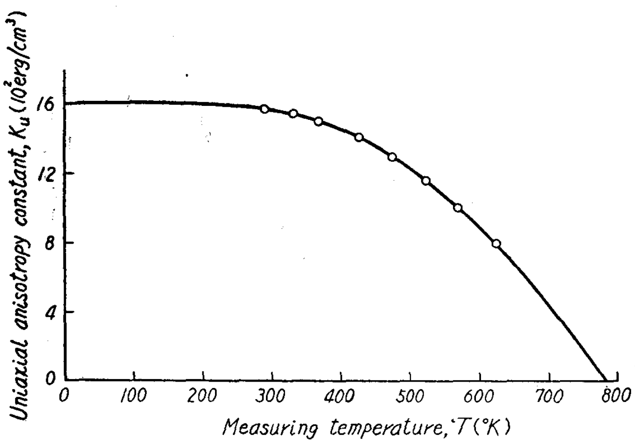

Fig. 12. Measuring temperature dependence of the uniaxial magnetic anisotropy induced by annealing in magnetic field of about 1700 Oe at 450°C for 5 hours in a (1$\bar{1}$0) disc of 12 %Co-Ni single crystal. A solid curve represents a calculated $(I_T/I_0)^2$ curve.

and $K_2=2.98\times10^3$ erg/cm³.

The magnetic torque curves measured at various temperatures are shown in Fig. 11. The dependence of K_u on the measuring temperature, T, as obtained from the analysis of the measured torque curves is shown in Fig. 12. It is to be noted that the measured K_u values are not plotted beyond about 350°C in Fig. 12. This is because the induced magnetic anisotropy changes during the torque measurement above this temperature or so. For example,

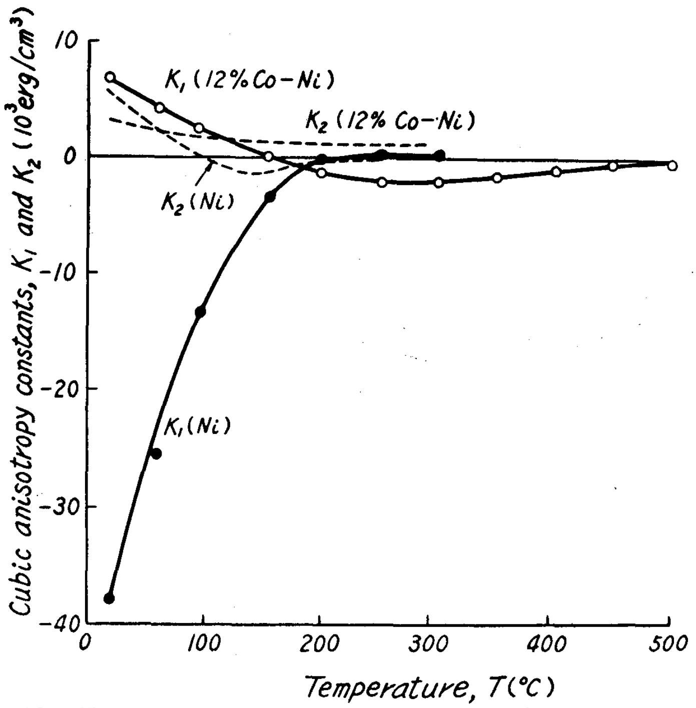

Fig. 13. Temperature dependence of the cubic ferromagnetic anisotropy constants, K_1 and K_2, in 12% Co-Ni alloy and in nickel.

when the magnetically annealed specimen disc was heated, without an applied magnetic field, at about 350°C for 40 minutes, which was the time necessary for the completion of the torque measurement, the resulted decrease in K_u at room temperature was found to be about 20% in magnitude.

However, even above 350°C, we can determine accurately values of the cubic magnetic anisotropy constants, K_1 and K_2, from Fourier analysis of the measured torque curves in the same way as at lower temperatures. Thus determined K_1 and K_2 values for various temperatures of 12 %Co-Ni alloy are shown in Fig. 13. Fig. 13 also contains the data of the temperature dependence of K_1 and K_2 in nickel, which were measured, in this connection, with $(1\bar{1}0)$ disc single crystal prepared from electrolytic nickel by the same procedure as for 12% Co-Ni disc single crystal. As seen from this figure that K_1 of 12 %Co-Ni alloy changes its sign from positive to negative at about 150°C, while that of nickel becomes slightly positive at temperatures above about 200°C. That K_1 of nickel seemingly showed such a temperature dependence was suggested previously by Kirkham[15] from the analysis of the magnetization curves of nickel single crystals measured by Honda, Masumoto, and Shirakawa.[16] Thus, the temperature dependence of K_1 shows a complicated trend similar to its alloy composition dependence at room temperature mentioned before. Nevertheless, K_u changes monotonously with temperature (Fig. 12), indicating that K_u is not originated from the ordinary magnetocrystalline anisotropy. Fig. 13 shows further that K_2 of 12 %Co-Ni alloy is positive at

(15) D. Kirkham: Phys. Rev., **52** (1937), 1162.

(16) K. Honda, H. Masumoto and Y. Shirakawa: Sci. Rep. Tôhoku Imp. Univ., **A 24** (1935), 391.

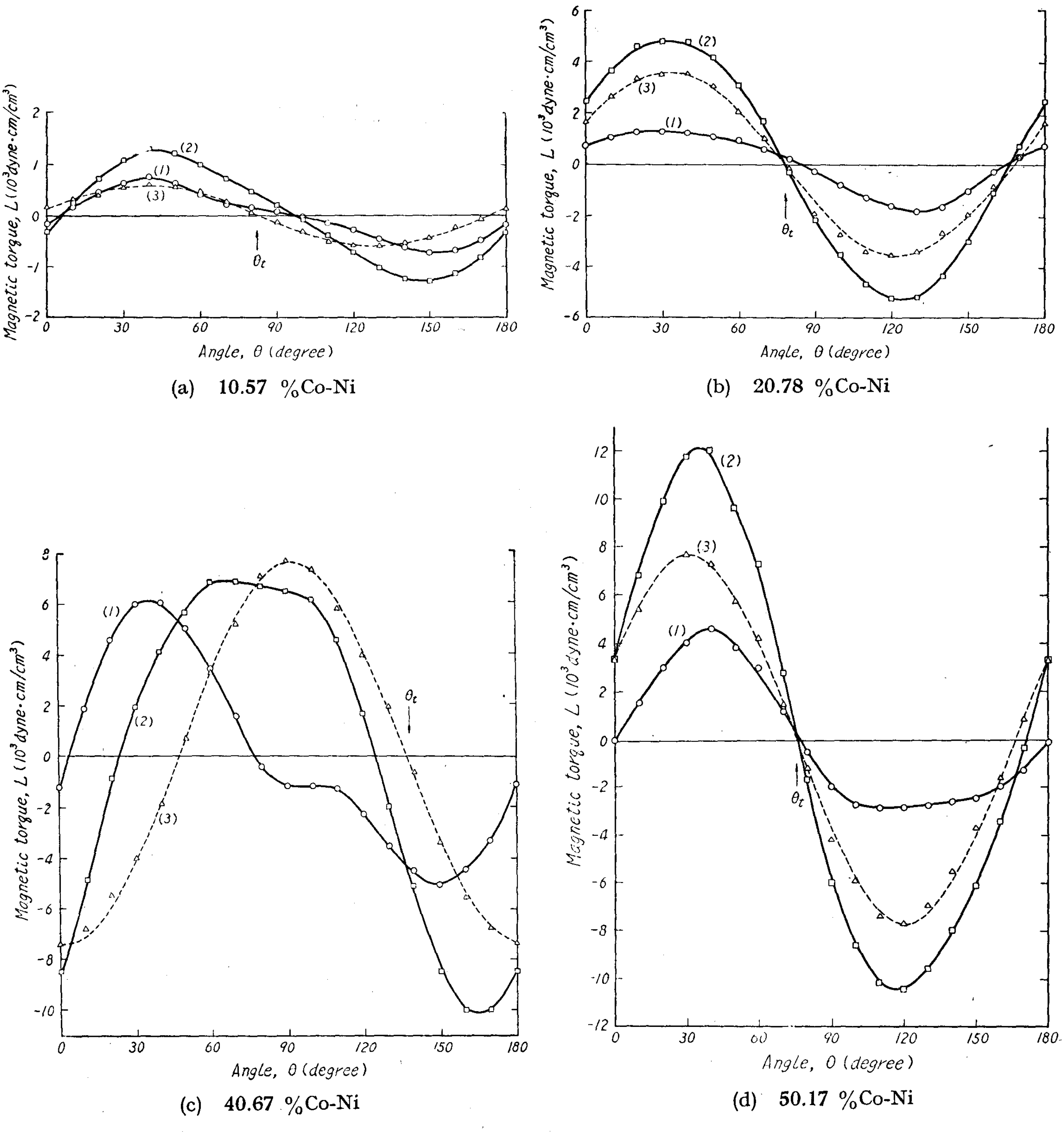

Fig. 14. Magnetic torque (L) curves in variously heat-treated states of polycrystalline discs of 10.57, 20.78, 40.67, 50.17, and 60.20 %Co-Ni alloys.

Curve (1) : cooled from above the Curie temperature in the absence of an applied magnetic field,

curve (2) : annealed at 400°C for 30 hours in the presence of an applied magnetic field of about 2410 Oe,

△ : (2) − (1),

curve (3) : calculated from $L = -K_u \sin 2(\theta - \theta_0)$, where $\theta_0 = \theta_t$.

all temperatures, but that of nickel changes from positive to negative at about 100°C.

(3) Alloy composition dependence of the induced magnetic anisotropy.

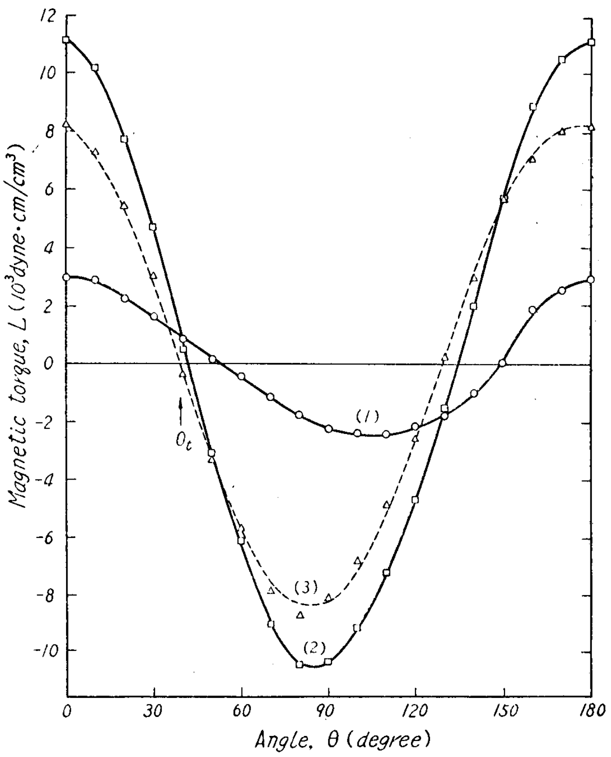

Fig. 14. (e) 60.20 %Co-Ni

Polycrystalline discs of 10.57, 20.78, 30.84, 40.67, 50.17 and 60.20 %Co-Ni alloys were used for the study of the alloy composition dependence of the induced uniaxial anisotropy. If the orientation distribution of crystal grains within the specimen is isotropic, the magnetic torque in the state annealed without magnetic field must be zero, but, actually, our specimen disc showed the magnetic torque after annealed without magnetic field. However, since, fortunately, the magnetic torque as measured in the state annealed without magnetic field was relatively small and did not change by repeated annealing, we could determine the induced magnetic anisotropy by subtracting it from the magnetic torque as measured in the state annealed in the presence of applied magnetic field.

The magnetic torque curves measured in magnetic field of 1050 Oe, which is strong enough to attain saturation (cf. Table 1), are shown in Figs. 2 and 14. Curves (1) in Fig. 14. are the torque curve measured in the state cooled rapidly from the temperature about 50°C higher than the Curie temperature in the absence of an applied magnetic field and curves (2) refer to the state annealed at 400°C for 30 hours in the magnetic field of 2150 Oe after heated at the temperature about 50°C higher than the Curie temperature, furnace-cooled to 400°C, and then rapidly quenched. In the latter case, the disc specimens were preliminarily heated at the temperature 50°C above their Curie points for 30 minutes and then cooled in the furnace to 400°C, where they were kept for 15 minutes before the annealing magnetic field was applied. The open triangles are the difference between the measured torque values of the curves (1) and (2). They lie well on the dashed curves (3) calculated from Eq. (1), and show that $\theta_0=\theta_t$, namely the direction of easy magnetization coincides with that of magnetic field applied during annealing. The K_u values obtained from curves (3) are plotted against the alloy composition as open circules in Fig. 15, where the results obtained for the state cooled at the rate of 200°/hr in the presence of magnetic field of about 1700 Oe are also plotted as open triangles.

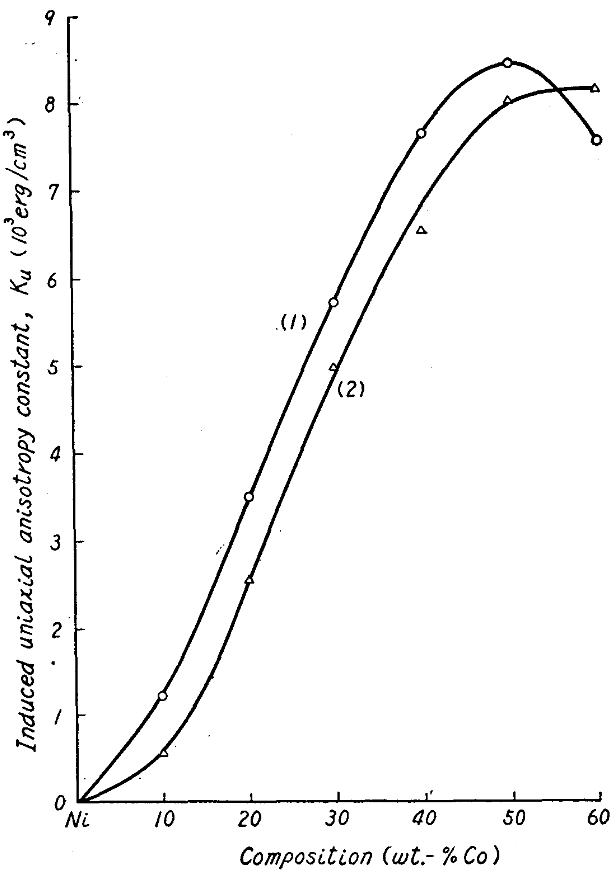

Fig. 15. Alloy composition dependence of the induced ferromagnetic anisotropy constant in magnetically annealed polycrystalline face-centered cubic nickel-cobalt alloys.

(1) : magnetically annealed at 400°C for 30 hours, and (2) : cooled in magnetic field at the rate of 200°C/hr.

IV. Discussions

As already mentioned in the introduction, the origin of the magnetic anisotropy induced by magnetic annealing in cubic ferromagnetic solid solutions has been studied by many investigators, and a good success has recently been achieved by the so-called directional order theory presented by Taniguchi-Yamamoto[8] and, independently, by Néel.[9] However, at that time, experimental data systematic and comprehensive enough to test this theory in detailed points were not available.

Now, we discuss the results of our measurements from the view point of directional order theory. Between atoms in ferromagnetic metal crystals, there exists, besides the ordinary exchange interaction, an anisotropic interaction. This interaction may be of the anisotropic exchange type and it may be expressed approximately in the form of superposition of dipole-dipole, quadrupole-quadrupole, and higher-order couplings. The dipole-dipole coupling can not appear in monatomic cubic crystals, since, in the cubic array of atoms of the same kind, this interaction is independent of the direction of magnetization. This also holds for cubic solid solution crystals, if the distribution of atoms of different kinds in them is isotropic. However, if a solid solution crystal is brought to a high temperature (below the Curie temperature) where the diffusion of atoms can take place, the distribution of atoms may change so as to lower the anisotropic interaction energy. Following this idea, Taniguchi-Yamamoto[8] and Néel[9] calculated the induced magnetic anisotropy energy, E_u. The result obtained by the former authors for an ideal dilute solid solution crystal is

$$E_u = -An^2 \left\{(I_\Theta/I_0)^2 (I_T/I_0)^2/\Theta\right\} \left\{\sum_i \alpha_i^2 \beta_i^2 + k \sum_{j>i} \alpha_i \alpha_j \beta_i \beta_j\right\}, \qquad (3)$$

where A is a constant depending on the type of crystal lattice, n is the solute concentration of solid solution, I_T, I_Θ, and I_0 are the values of the saturation magetization at the measuring temperature, $T(°K)$, at the annealing temperature, $\Theta(°K)$, and $0°K$,respectively, α_i's and β_i's ($i=1, 2, 3$) are the direction cosines referred to the crystal axes of magnetization vectors during the measurement and during magnetic anneal, respectively, and k is a numerical factor depending on the type of crystal lattice and on the range of interaction between atoms concerned, which is 4 for face-centered cubic structure if only the coupling between nearest neighbor atoms is taken into account. The expression of E_u for pseudo-isotropic polycrystal is obtained, by taking the average of Eq. (3) for all possible values of α_i's and β_i's, as

$$E_u = -A' n^2 \left\{ (I_\Theta/I_0)^2 (I_T/I_0)^2/\Theta \right\} \cos^2(\theta-\theta_0)\,, \tag{4}$$

where A' is a constant depending on the type of crystal lattice and on the range of interaction of atoms. Since, Eq. (4) is equivalent with Eq. (2), we have

$$K_u = -A' n^2 \left\{ (I_\Theta/I_0)^2 (I_T/I_0)^2/\Theta \right\}\,. \tag{5}$$

It is to be noted that the expression of E_u for $(1\bar{1}0)$ disc single crystal is also the same as Eq. (4).

Firstly, to test whether the dependence of the induced magnetic anisotropy on the temperature, Θ, of magnetic anneal measured with polycrystalline 30.84% Co-Ni alloy accords with Eq. (4) or (5) or not, we have calculated const.$\times(I_\Theta/I_0)^2/\Theta$ by taking values of I_Θ/I_0 as the values of the Brillouin function

$$B\left(\frac{\mu H}{k\Theta}\right) = \frac{2S+1}{2S} \coth \frac{2S+1}{2S} \cdot \frac{\mu H}{k\Theta} - \frac{1}{2S} \coth \frac{1}{2S} \cdot \frac{\mu H}{k\Theta} \tag{6}$$

for $S=1/2$, where S is the total spin quantum number, μ the magnetic moment, H the molecular field, and k the Boltzmann constant, since Went(17) showed that the temperature dependence of the saturation magnetization of nickel-cobalt alloys can be described well by the Brillouin function for $S=1/2$. The calculated data is plotted as a solid curve in Fig. 6, which shows that the measured data accords well with Eq. (4) or (5).

Next, to compare the dependence of the induced magnetic anisotropy on the measuring temperature measured with $(1\bar{1}0)$ disc single crystal of 12 %Co-Ni with Eq. (4) or (5), we have calculated const.$\times(I_T/I_0)^2$ by taking values of I_T/I_0 as the values of the Brillouin function (6), in which $S=1/2$, Θ is replaced by T, and by taking the Curie temperature as 783°K. The calculated data is plotted as a solid curve in Fig. 12, indicating that the measured data accords well with Eq. (4) or (5).

Finally, we compare the alloy composition dependence of the induced magnetic anisotropy with directional order theory. As shown above, the induced uniaxial ferromagnetic anisotropy depends on the magnetic annealing temperature, Θ, as well as on the measuring temperature, T, in the form of $K_u \propto (I_\Theta/I_0)^2 (I_T/I_0)^2/\Theta \cdot$

(17) J.J. Went: Physica, **17** (1951), 99.

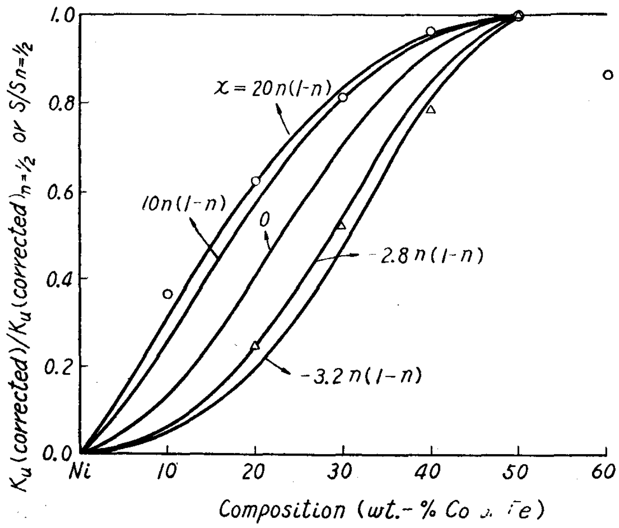

Fig. 16. Alloy composition dependence of the induced uniaxial ferromagnetic anisotropy, corrected for the alloy composition dependence of the Curie temperature, as compared with directional order theory.

○ : the present measured data with Ni-Co alloys, and

△ : Fergusson[13]'s measured data with Ni-Fe alloys.

I_Θ/I_0 and I_T/I_0 vary, respectively, with Θ/T_c and T/T_c, where T_c is the Curie temperature. Thus, $(I_T/I_0)^2(I_\Theta/I_0)^2/\Theta$ is a function of Θ, T, and T_c, and T_c is a function of the alloy composition. Accordingly, in order to find the true composition dependence of the induced uniaxial anisotropy, the measured K_u values must be corrected for the composition dependence of the Curie temperature, T_c. We have made this correction by dividing the measured K_u values by the values of $(I_T/I_0)^2(I_\Theta/I_0)^2/\Theta$ for various alloy compositions, which have been computed taking the values of the Brionllin function (Eq. (6)) for $S=1/2$ at $T/T_c=$ 400°C$/T_c$ and 20°C$/T_c$ as the values of I_Θ/I_0, and I_T/I_0, respectively. Thus corrected K_u values are plotted as open circles in Fig. 16, where the corrected K_u value for 50 at. -%Co is chosen to be unity.

On the other hand, Néel[9] has shown that, if the solid solution is not dilute and not ideal, n^2, in Eq. (3) should be replaced by

$$S = 4\,n^2\,(1-n)^2 \exp\,(-v/k\,\Theta)/(1+x)^{1/2}\,\{1+(1+x)^{1/2}\}^2\,, \tag{7}$$

where

$$x = 4\,n\,(1-n)\,\{\exp\,(-v/k\,\Theta)-1\}\,. \tag{8}$$

S reduces to $n^2(1-n)^2$ when the ordering energy $v=v_{aa}+v_{bb}-2v_{ab}=0$. In Fig. 16, the corrected K_u or S values are plotted against the alloy composition, n, for cases of $x=0(v=0)$, $20n\,(1-n)$, $10n\,(1-n)$, $-2.8n\,(1-n)$, and $-3.2n\,(1-n)$. Our measured data with polycrystalline nickel-cobalt alloys, shown by open circles in the same figure, are well fitted to the curve for $x=20n(1-n)$. Using this values of x, we have estimated the ordering energy of nickel-cobalt alloys from Eq. (8) and obtained the value $v=-1.67\times10^{-13}$ erg. The negative sign of this value of the ordering energy indicates that nickel-cobalt alloys are of the precipitation type. The critical temperature, T_c, of the precipitation for $n=0.5$ has been estimated to be about 3200°K from the relation $kT_c/|\,v\,|=2.69$ derived under the quadruplets approximation.[18] Actually, however, we have no evidence of precipitation with nickel-cobalt alloys. For the sake of comparison, the measured data obtained

(18) E.A. Guggenheim : *Mixtures*, p. 59.

by Ferguson[19] with face-centered cubic nickel-iron alloys are also plotted in Fig. 16. The ordering energy of nickel-iron alloys, determined from Eq. (8) is positive, indicating that these alloys are of the ordering type, and the critical temperature for Ni_3Fe alloy is estimated to be about 360 or 480°K from the relating $kT_c/v=0.411$,[20] taking $x=-2.8n(1-n)$ or $-3.2n(1-n)$. These values of the critical temperature for superlattice Ni_3Fe are only somewhat smaller than the value of 770°K found experimentally.

Thus, Eqs. (7) and (8) derived by Néel[9] represent the experimental facts qualitatively fairly well, but quantitatively a fairly well agreement is obtained only for nickel-iron alloys. This may be due to the circumstance that the atomic interaction is not rigorously taken into account in Néel's calculation and, in particular, to the fact that the atomic interaction is assumed to change only the number of atom pairs which contribute to the induced magnetic anisotropy, the effect of the atomic interaction on the arrangement of atom pairs being completely ignored. This feature also appears in the crystal orientation dependence of the induced magnetic anisotropy, which is reported by Aoyagi[11] in the suceeding part of this paper.

Summary

We have studied systematically the character of the induced magnetic anisotropy in face-centered cubic Ni-Co alloys which may be regarded as one of the most ideal solid solution systems. The magnetic anisotropy was measured by a torque magnetometer designed specially for high-temperature measurements, and the magnetic anneal of the disc specimen was done as it was mounted on the torque magnetometer.

The dependence of the induced magnetic anisotropy on the temperature and duration of magnetic anneal was studied with 30.84 %Co-Ni alloy polycrystal. It has been found that the magnetic anisotropy energy, E_u, induced by mangetic anneal is uniaxial and its direction of easy magnetization is parallel to that of an applied magnetic field during annealing. Generally, as the duration of magnetic anneal increases, E_u increases quickly at first and then more and more slowly, finally attaining to saturation, and as the temperature of magnetic anneal becomes higher, the rate of development of E_u increases, while its saturation value decreases. The development of E_u can not be described in terms of single relaxation time and the associated relaxation times become longer as the duration of magnetic anneal increases. The dependence of E_u on the temperature, Θ, of magnetic anneal can be expressed well by an expression $E_u=\text{const.}\times(I_\Theta/I_0)^2/\Theta$, where I_Θ and I_0 are the values of the satruation magnetization at Θ(°K) and 0°K, respectively, which was derived by Taniguchi and Yamamoto from the so-called directional order theory.

The dependence of E_u on the measuring temperature, T, was studied with

(19) E.T. Ferguson, Compt rend., **244** (1957), 2363; J. Appl. Phys., **29** (1958), 252.
(20) E. A. Guggehheim : *Mixture*, p. 141.

an $(1\bar{1}0)$ disc single crystal of 12 %Co-Ni alloy and the observed dependence was found to be expressed well by a relation E_u=const. $\times(I_T/I_0)^2$, where I_T is the values of the saturation magnetization at T (°K), which was derived by Taniguchi and Yamamoto from the stand point of directional order theory. In connection with this study, the temperature dependence of the cubic magnetocrystalline anisotropy constants, K_1 and K_2, was measured with 12 %Co-Ni alloy and pure nickel, and it has been found that, as the temperature rises, K_1 of 12 %Co-Ni alloy changes from positive to negative at about 150°C, while K_1 of nickel shows small positive values above 200°C and that K_2 of 12 %Co-Ni alloy is always positive, while K_2 of nickel changes from positive to negative at about 100°C.

The alloy composition dependence of E_u was studied with polycrystalline discs of 10.57, 20.78, 30.84, 40.67, 50.17, and 60.20 %Co-Ni alloys, and it has been found that E_u changes with increasing cobalt content, n, approximately as $n^2(1-n)^2$ and shows a peak value of 8.4×10^3 erg/cm^3 at about 50 %Co. The comparison of the measured data as corrected for the composition dependence of the Curie temperature with Néels theoretical formula indicates that the ordering energy of Ni-Co alloys is negative and, hence, the alloys are of the precipitation type. It is to be noted that a rather pronounced deviation from a $n^2(1-n^2)$ curve predicted for ideal solid solution has been found, which may be considered as due to rather simplified assumptions, employed in the directional-order theory, concerning contributions from neighbor atoms and the influence of the deviation from ideal soild solution.

In closing, the present authors express their hearty thanks to Prof. S. Chikazumi, Research Institute for Solid State Physics, Tôkyo University, who gave them an important suggestion for the construction of the torque magnetometer and to Assist. Prof. T. Iwata in our research department, who gave them valuable comments during the course of this work.