Temperature and Pressure Dependence of Magnetocrystalline Anisotropy of Gadolinium and Gadolinium-Yttrium Alloys

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CONTENTS

ABSTRACT

Generally speaking, in rare earth metals, the 4f shell is magnetic and the spin-orbit interaction in it is larger than that of the 3d transition metals because the orbital angular momentum is not quenched. A strong magnetocrystalline anisotropy is produced in rare earth metals through the interaction between this nonzero orbital angular momentum and the electrostatic field produced by the surrounding atoms.

In the case of gadolinium (Gd), the magnetocrystalline anisotropy energy is very small compared with that of other rare earth metals, since Gd atom has no orbital magnetic moment. The temperature dependence of the anisotropy constants of Gd, however, has two remarkable features; (i) the dominant term of the anisotropy energy shows a complicated temperature dependence, changing the sign twice below the Curie point, (ii) some part of the anisotropy energy is reserved above the Curie point (293°K) to about 360°K.

The purpose of this paper is to investigate the origin of this complicated anisotropy. The present work is mainly concerned with the following two subjects; (i) saturation magnetization, magnetic susceptibility and the temperature dependence of the anisotropy energy of gadolinium-yttrium,

(ii) the temperature- and the pressure-dependence of the magnetocrystalline anisotropy of Gd. The close similarity of Gd and yttrium (Y) in structure and atomic dimensions indicates that Y should be a good diluent for Gd.

The experimental value 7.55 μ_B of the saturation moment for pure Gd is significantly higher than the value 7.00 μ_B obtained from the spin angular momentum. The difference between these two values, 0.55 μ_B, is considered to be due to the polarization of the conduction electrons. The introduction of Y into Gd increases the magnetic per Gd atom. The increase of the saturation moment per Gd atom in Gd-Y alloys will depend upon the conduction electrons of Y amounting to 0.20 μ_B.

The addition of non-magnetic constituent Y causes a drastic change in the temperature dependence of the anisotropy of Gd-Y alloys. For instance, the anisotropy constant of 30 at.% Y(about 13×10^5 erg/cc) is larger than the value (about -8×10^5 erg/cc) for pure Gd at 0°K.

The temperature dependence of the anisotropy of pure Gd under hydrostatic pressure exhibits a very complicated behavior and shifts towards low temperature side.

Summing up above results, it was concluded that;

(A) the polarization of the conduction electrons contributes to the magnetization,

(B) the change of the anisotropy in Gd-Y alloys can not be explained by the change of the magnetic moment,

(C) the anisotropy due to the dipole-dipole interaction was estimated by Brooks et al., the calculated value by them shows about -5×10^5 erg/cc and the experimental value in the present work exhibits about -11×10^5 erg/cc.

The magnetocrystalline anisotropy of Gd will depend on the contributions from both the conduction electrons related to (A) and (B) and from the 4f localized elecrtrons due to (C).

The apparent anisotropy of the Y was estimated from the difference values between Gd-Y alloys and pure Gd. Y is non-magnetic so that the anisotropy will be caused by the conduction electrons. The anisotropy due to the conduction electrons could be estimated, provided that the constribution of the conduction electrons from Y is the same as that of Gd.

In conclusion, the magnetocrystalline anisotropy of Gd is considered to be caused by two terms, i.e., localized 4f electrons and conduction electrons.

Chapter 1 : PREFACE

Magnetocrystalline anisotropy have been studied from both experimental and theoretical point of view. It revealed that for ionic crystal's theory is generally in good agreement with experiment. For metals, however, there remain many unsolved problems.

Generally, magnetrocrystalline anisotropy arises from the coupling between the electron spin and the orbital motion of the electron . The directional properties of the electron orbits are highly oriented with respect to the crystal lattice, so that the effect of an applied magnetic field on the spin moments depends on spin orientation with respect to the crystal lattice.

For the theoretical works on the magnetocrystalline anisotropy, the most important and remarkable work is the one by Van Vleck issued in 1937.[1] In that study, he proposed a model called 'localized spin model' in order to explaine the anisotropy of metals (especially for Fe, Co, Ni). After that, Nagamiya et al.[2] and Yosida et al.[3] developed the theory of Van Vleck and extended their theories to include the anisotropy of the ionic crystals.

The origin of the anisotropy of ionic crystals can be

explained by interatomic dipole-dipole interaction, intra atomic dipole-dipole interaction, and spin-orbit coupling as a small perturbation from the free ion state, since the electrons in ionic crystals are well localized.

On the other hand, for the iron group metals and their alloys, the theory is not yet complete, though some theories, such as the band theory[4,5] or localized ion model, have been successful in at least a qualitative explanation of the anisotropy.

Research of the magnetism of the rare earth metals has not so long a history as for the 3d transition metals. However, recent work [6~16] shed a light on the understanding of the anisotropy. Rare earth metals have various characteristic magnetic properties, and one of the most outstanding properties are their very strong uniaxial magnetocrystalline anisotropy.

The anisotropy energy of the rare earth metals except gadolinium (Gd) has been measured to be on the order of 10^8 erg/cc.[17~19] These values are $10^2 \sim 10^4$ times larger than those of ferromagnetic 3d transition metals, such as Fe, Co or Ni. The large difference of the values between the two groups can be fairly well understood through the following

considerations. In the rare earth metals, the magnetic properties depend mainly on the 4f electrons whose orbits are very near the atomic core, therefore even in the crystalline state, the 4f electrons feel little effect from the surrounding ions, and conserve their orbital angular momentum, resulting from the fact that the spin-orbit interaction in rare earth metals is stronger than that of the 3d transition metals.

Such a strong anisotropy is a very important factor to explain the various magnetic properties, especially in the problems of the magnetic ordering of the rare earth metals[20~22]. In reality, however, it is difficult to make an accurate measurement of the anisotropy energy experimentally, because a magnetic field larger than 10^6 Oe is necessary in order to rotate the magnetization.

Even if we could successfully obtain such an intense magnetic field, when this high field is applied to Tb and Dy in order to rotate the magnetic moments, the bulk crystals in often plastically deformed[23,24], so the anisotropy energy is impossible to determine exactly.

Tajima and Chikazumi[25~27] have succeeded in measuring the anisotropy energy of rare earth metals by doping them into

Gd which has a comparatively small anisotropy energy. They utilized the fact that the isolated spin of the doped rare earth metal in the host Gd metal is easily rotated by a comparatively low external magnetic field. According to them, the heavy rare earth metals except Gd can be understood through the one-ion model.

On the other hand, Gd has an small anisotropy among the rare earth metals because of the zero orbital angular momentum in the ground state, which has already been measured by sevral workers[28~32].

The spin structure of Gd is simple ferromagnetic and the structure of crystal is hexagonal closed-packed as other rare earth metals.

The main purpose of this work is to study the origin of the anisotropy of Gd, which has a rather simple magnetic structure compared with that of other rare earth metals and has been studied by many workers.

It can be expected that our study of the origin of the magnetic anisotropy of Gd will play the role of an intermediary step toward the better understanding of the anisotropy of the transition metals whose origin has not yet been made clear. This is because Gd has zero orbital angular momentum, but other rare earth metals have non zero value, and further more the magnitude of this anisotropy can be compared with 3d transition metals as Fe, Co and Ni, whose orbital angular

momentum L is supposed to be quenched in the metal.

If 'one-ion model' is assumed for the anisotropy of Gd, the doping of the non-magnetic yttrium (Y) metal should reduce the magnetization and the anisotropy energy of the alloy. To investigate this speculation, the author has studied the temperature dependence of the anisotropy of Gd-Y alloys and the pressure dependence of the anisotropy of Gd.

The reason that Y was chosen as the duluting material is that it has almost the same crystal structure (h.c.p), lattice parameter, atomic volume, electronic state (valence +3) as Gd, so that the introduction of Y increases the average Gd-Gd distance and gives a certain effect on the atomic interactions between Gd atoms.

In chapter 2, it will be described, at first, of the preparation methods of Gd and Gd-Y alloy single crystals used in this experiments, and next, it will be described of the apparatus used for the measurement of torque, magnetization and magnetic susceptibility, and last a description will be described of the high pressure vessel used for torque measurements under high pressure.

In chapter 3, it is given the results of the following two experiments carried out to study the magnetic anisotropy of Gd.

i) Temperature dependence of magnetization, magnetic susceptibility and magnetic anisotropy for Gd-Y alloys.

ii) Temperature and pressure dependence of magnetic anisotropy of pure Gd.

In chapter 4, it will be discribed of the properties of Gd and Y (such as lattice parameter, density of states and so on), and it will be discussed on the origin of the anisotropy of Gd.

Chapter 2 : SPECIMEN PREPARATION and EXPERIMENTAL APPARATUS

2.1. Specimen Preparation

Rare earth metals used this experiment were bought from two companies :

Lunex Company	(U.S.A.)
A.P.C.Co.	(U.S.A.) .

The purity of all specimens was 99.9%. All single crystals were made by the following re-crystalization method[33];

(i) Samples, about 5∿8g weight, were melted in an arc furnace in an atmosphere filled with argon gas. In the process, samples were turned over about 5 times in order to promote uniformness of the samples. This procedure is especially important for alloys. Thus, button shaped ingots, about 10∿15 mmϕ, were obtained.

(ii) Then, the samples were sealed into quartz tubes filled with argon gas. Samples were wrapped with tantalum foil in order to prevent the reaction of samples with the quartz wool.

(iii) The sealed samples were annealed for a day at temperatures (1180°c for the case of pure gadolinium) about 120∿150°c below the melting temperature (1312°c for Gd). In these processes, the author observed excellent crystallization of the samples both for pure Gd and Gd-Y alloys. In several cases, the whole ingot revealed itself to be in a single crystal state. The weight of samples was measured before

and after these processes and it was found, in all cases, that no appreciable decrease of the total weight occured. It was found that the principal axis of the crystal (c-axis) is nearly perpendicular to the face of ingots. One may suppose that the crystal growth occurs so as to make the c-axis parallel to the direction of the arc.

The single crystals was cut from ingots obtained. Single crystals were shaped into spheres or disks. Specimens to be used for torque measurements were shaped into sheres of 2.5∿3.5 mm by the two-pipe-lapidary method[34,35] in order to eliminate shape anisotropy. Surface strains were eliminated by chemical etching using ethyl alcohol plus 10% nitric acid solution. Approximate directions of the crystal axis were found by the reflection of light from the surface of the specimens, but then the direction of the axis was determined by a back Laue camera within an accuracy of $\pm 1°$. The specimen was set into the holder of torque apparatus within this accuracy. Purities of specimens used in this experiment are shown in Fig. (2.1). Purities are sufficient for this reserach. Measurements of the magnetic susceptibiltiy and torque were made on these samples.

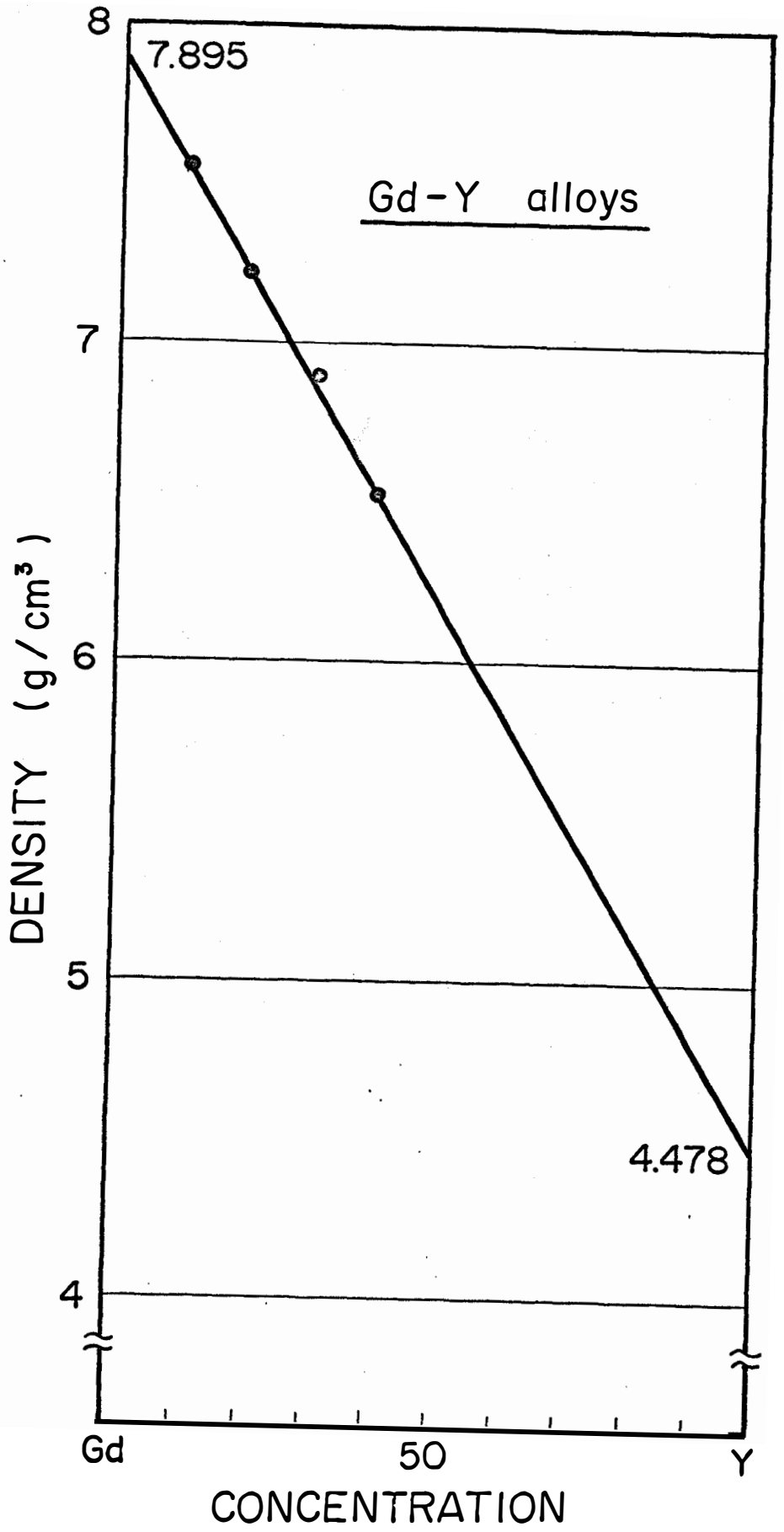

8
7.895
Gd-Y alloys
7
6
5
4.478
4
DENSITY (g/cm³)
Gd
50
Y
CONCENTRATION

Fig. (2·1)

2.2 Experimental Apparatus

(A) Torque Magnetometer

In order to measure the magnetocrystalline anisotropy, a conventional torque magnetometer was made using paper strain gauges which were developed so as to fit the measurement of rare earth metals by Tajima and Chikazumi.[36] That magnetmeter was modified so as to measure torque under high pressure with temperature changes.

Fig.(2.2) shows the schematic diagram of the paper strain gauge torque meter. The vertical specimen holder is made in the form of a phosphor bronze cylinder, 8mm in inner diameter and 10mm in outer diameter with 8 slits, 20mm in length and 1.5mm in width. The cylinder is properly flexible for twist, but rigid enough to prevent lateral motion of the specimen. Two cross-type paper strain gauges each of 4mm in length, having a gauge factor 1.95, were cemented directly on the opposite sides of the slitted portion and were connected to form a wheatstone bridge. A torque exerted on the specimen could be measured by amplifying the unbalance voltage of the wheatstone bridge through D.C. amplifier with a voltage gain of 26 to 46 db.

The sensitivity covers a range of 5×10^3 dyne-cm to 10^5 dyne-cm for a full scale torque within $\pm$ 1% error. The temperature of specimen is detected by a thermocouple of Au-Co vs. Cu. The electromagnet used in the torque measurement

is a large shell-core type,[37] and it produces a field up to maximum 32,000 Oe in a 5cm gap.

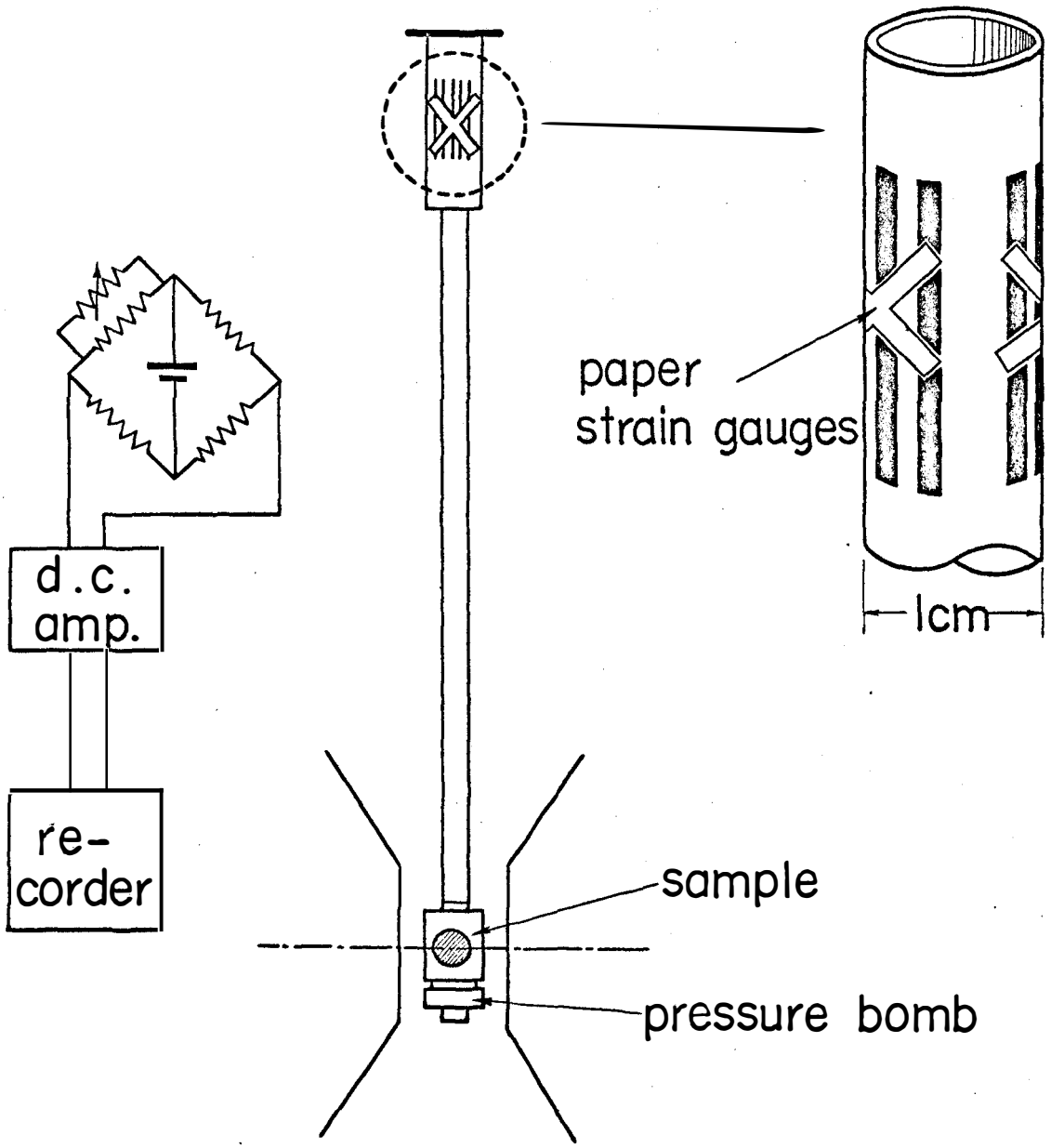


DIAGRAM OF TORQUE APARATUS

Fig. (2·2)

(B) Clamped type High Pressure Bomb

A small clamped-type of pressure bomb, which was developed by Sawaoka and Kawai,[38] was used for this measurement. Construction details are shown in Fig.(2.3). The pressure vessel is made of a hardened Cu-1.82% Be alloy. The pressure fluid was a 1 : 1 mixture of kerosene and electric transformer oil.

The pressure is measured by the use of a manganin gauge which was calibrated using the phase transition of ammonium fluoride (NH_4F) at 3631 bar/cm^2 at 25°C[39,40]. A typical calibration curve is shown in Fig. (2.4). The abrupt change of piston displacement corresponds to the phase transition. The curves show the existence of hysteresis which is caused by friction from packing materials around the piston. After the desired pressure was attained at room temperature, the piston was locked tightly to the cylinder (D) with an attached screw nut (B) and slowly cooled. The pressure values determined from manganin gauge observation at 201°K and 77°K are shown in Fig. (2.5) as junction of pressure clamped at 293°K. The oil pressure in the bomb showed only a very small decrease with decreasing temperature except when the oil congealed.

The pressure, P_{77}, obtained at 77°K, is expressed by the following equation

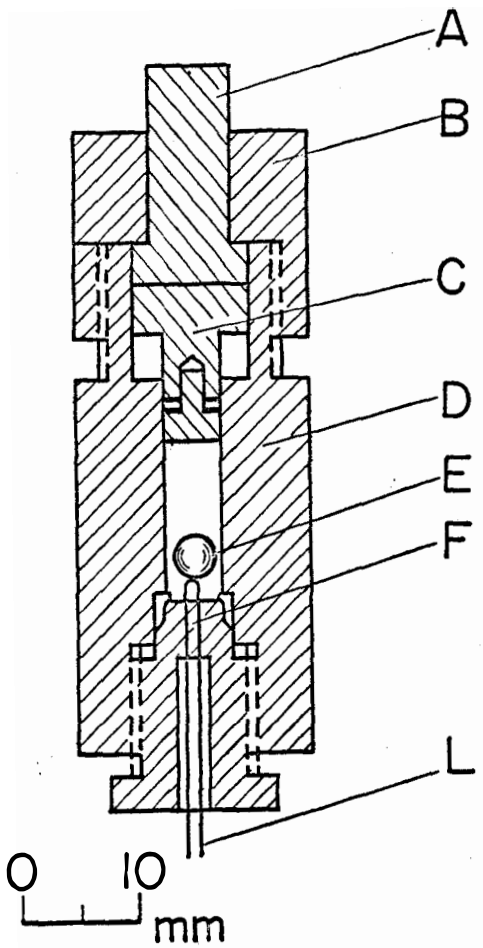
$$P_{77} = a (P_{rt} - P_f)$$

where P_{rt} is pressure value locked in at room temperature and P_f is constant value and, both values given by Sawaoka et al.[42] as follows

$$P_f : 3540 \text{ bar}$$

$$a : 1.07 .$$

The temperature of the bomb is controlled by the use of Cu-3% Al heater which was wound on the bomb.



Clamped Type of High Pressure Bomb

A — rod transmitting the force

B — locking nut

C — piston with mushroom type packing

D — bomb

E — sample

F — plug

L — thermocouple

Fig. (2·3)

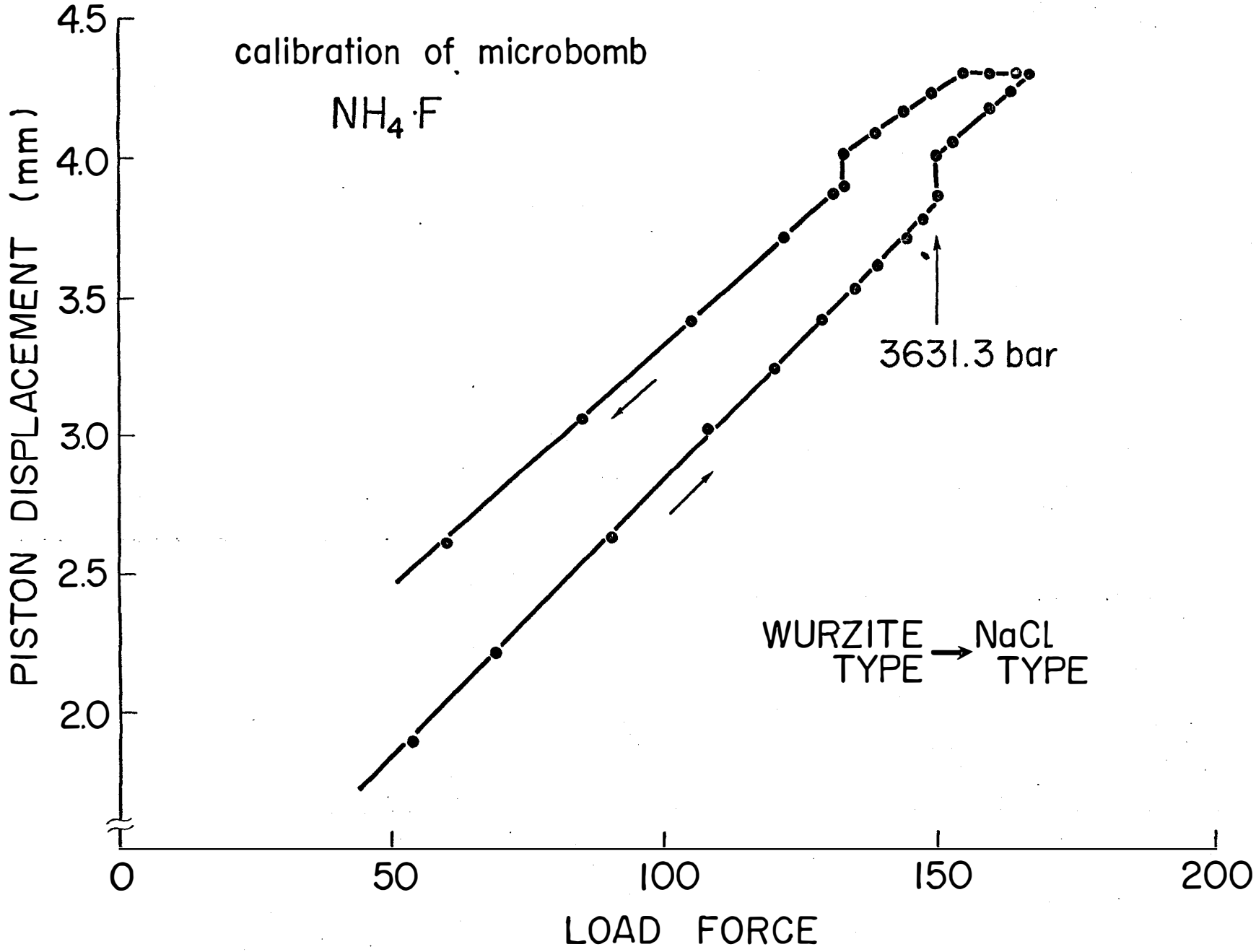

calibration of microbomb
$NH_4 \cdot F$
3631.3 bar
WURZITE TYPE → NaCl TYPE
PISTON DISPLACEMENT (mm)
4.5
4.0
3.5
3.0
2.5
2.0
0
50
100
150
200
LOAD FORCE

Fig. (2.4)

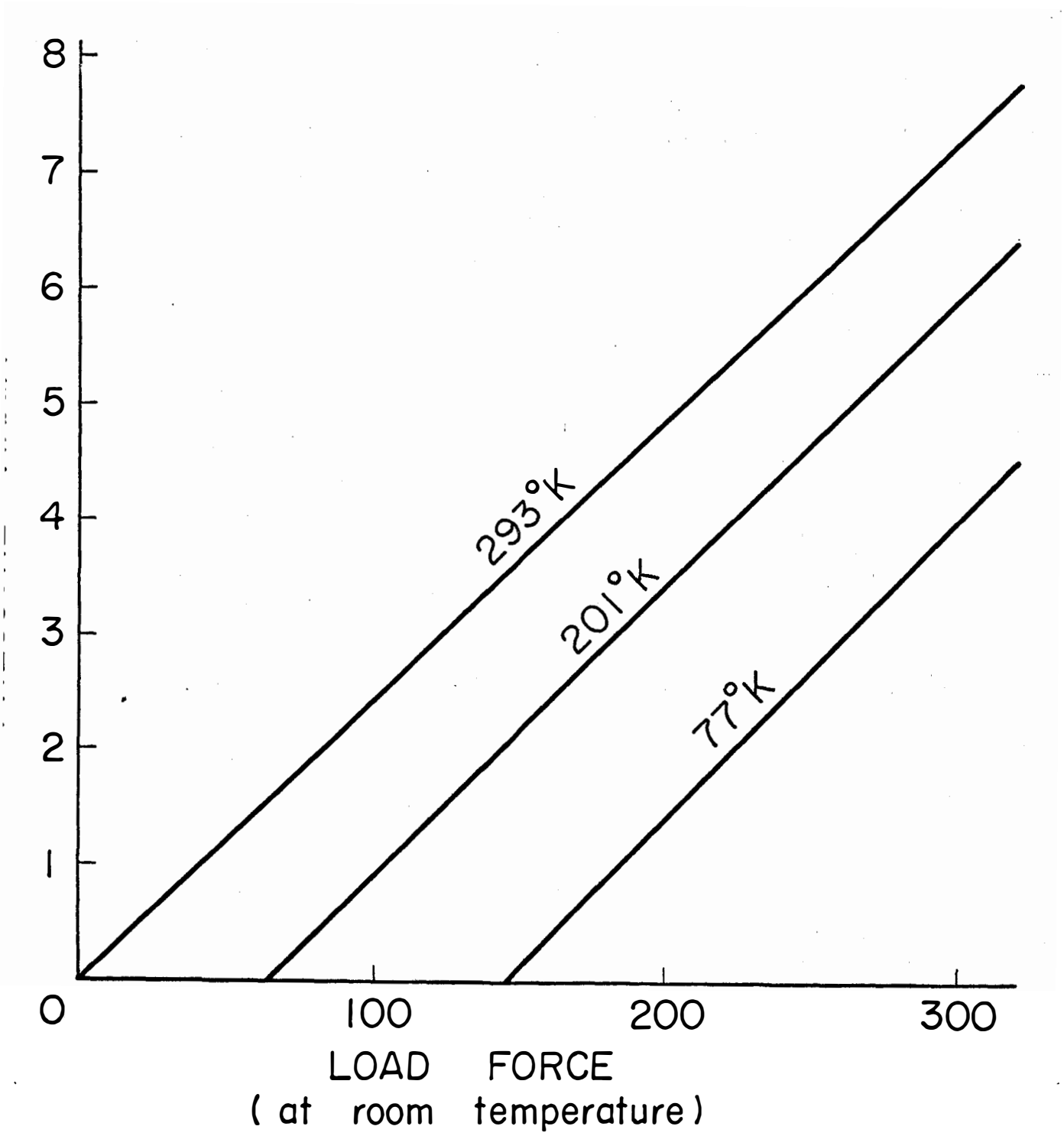

8
7
6
5
4
3
2
1
0
100
200
300
293°K
201°K
77°K
LOAD FORCE
(at room temperature)

Fig. (2·5)

(C) Ballistic Type Magnetometer

An electro-magnetic induction method was employed for the magnetization measurements. In this method, the magnetic moment M[Wb-m] of the specimen was detected as the electromotive force V[volt] induce in the pick up ciols. If the magnetic moment was moved near the pick up coil, the magnetic flux ϕ[Wb] through the coil changes. This change of the flux is related to the electromotive force through the formula :

$$-\frac{d\phi}{dt} = V$$

$$\phi = \alpha M$$

where α is constant which depend upon the apparatus and the shape of the sample. With this formula, the magnetic moment is determined by the integral

$$M = \frac{1}{\alpha} \int_0^t V\, dt. \qquad (2\text{-}1)$$

The block diagram of the magnetometer is shown in Fig. (2.6).

The sample is quickly displaced from the center of one Helmholtz coil to the center of the other Helmholtz coil and the associated total flux change is read by a digital volt-

meter of an integration type.

The sample rod is moved by a servo-moter and a crank is used as to change the rotational motion to translational motion. The gate of the digital voltmeter is opened just before the sample displacement begins and closed after the displacement is finished. The time of the sample displacement is 0.7 second, whereas the gate of the digital voltmeter is opened for a second; the total flux change is detected.

As the standard material, iron was used. The satuation magnetization of it is 220 emu/g. With the standard, the coefficient α in Eq.(2-1) is determined by substituting the value t=0.7 second. The scanner is a switch to read the values of the current of the super conducting magnet, of the magnetic field in the super conducting magnet, and of the induced signal independently. The superconducting magnet generates a field up to 63 k Oe. The author is indebted to Mr. Maruyama of Japan Electron Co. for his kindness in permitting the use of the mechanical parts that he made. The mechanical part is the essential part to move the sample rod.

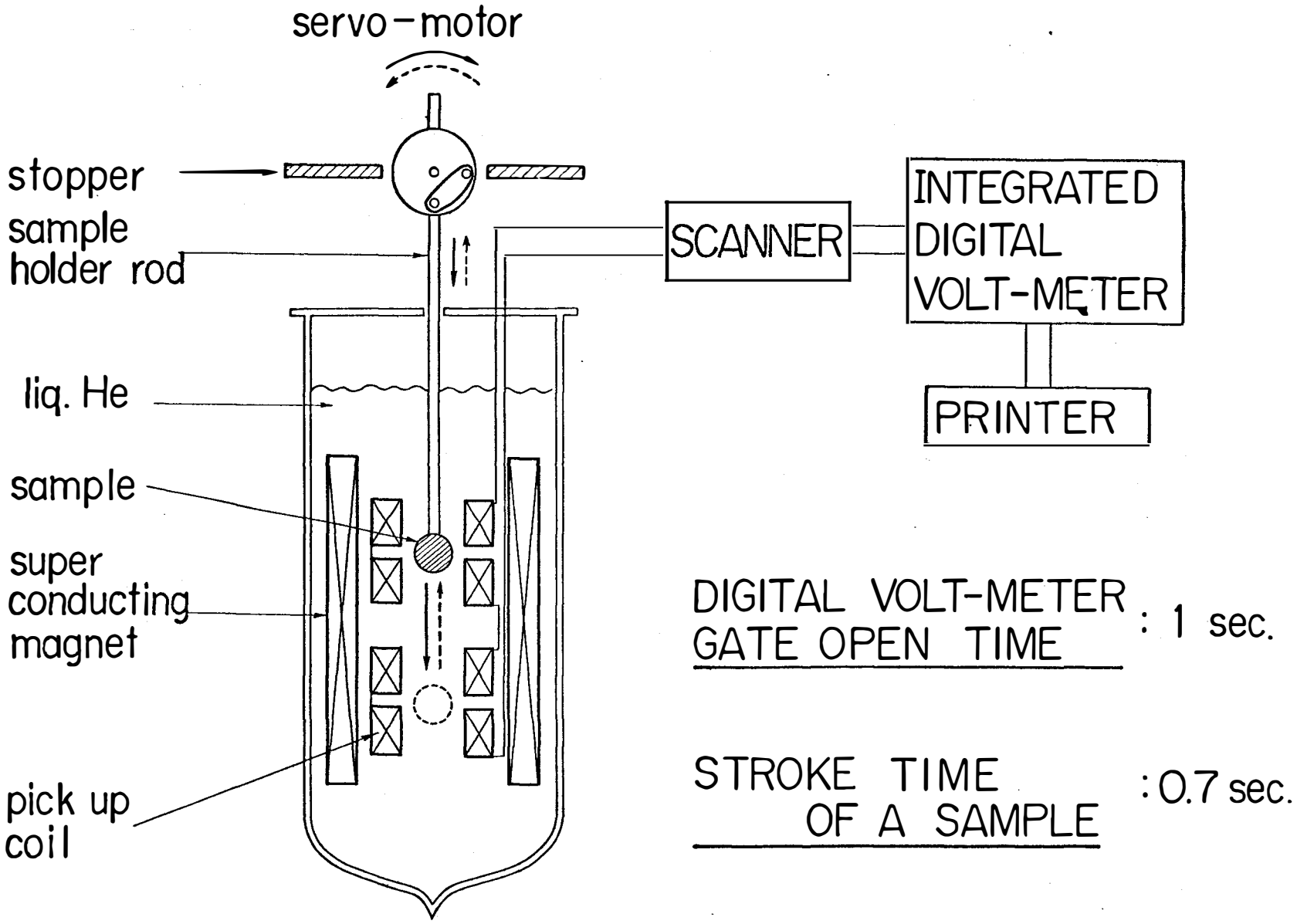


Fig.(2·6) BLOCK DIAGRAM OF MAGNETOMETER

(D) Pendulum Type Magnetometer

For the measurements of the magnetic susceptibiltiy, a pendulum type magnetometer was employed. The apparatus was made by Dr. T.Mizoguchi of Institute for Solid State Physics. This equipment was developed by Hirakawa[43,44]. This is of the Faraday type ; that is, it detects the force F that acts on magnetic materials in non uniform magnetic field,

$$F = M_x \frac{\partial H_x}{\partial Z} = m\sigma \frac{\partial H_x}{\partial Z} .$$

Here, M_x is the magnetic moment along the x-direction (the x-direction is defined as the direction of the line that connects the centers of the specimen, σ is the magnetization per unit mass, and H_x is the field along the x-direction. The Z-direction is perpendicular to the x-direction and the direction of the sample rod. The magnetization σ is determined by measuring the force F and the mass m using the above formula.

The principle of the pendulum type magnetometer is that the sample rod is supported by two sharp needles which are atached to the both ends of an arm. The arm is attached to the center of the sample rod. If we arrange the geometrical construction so as to make the center of mass of the rod come just below the fulcrum of the rod, the pendulum becomes very sensitive. Even a small external force at the end

point of the rod may couse a large inclination of the rod. The leaning of the rod is detected by a electrical capacitor attached at the top of the rod and this inclination is compensated by a negative feed back circuit.

Chapter 3 : EXPERIMENTAL RESULTS

3.1. Expansion of the Anisotropy Energy for Hexagonal close-packed Symmetry

The dependence of the free energy E of a ferromagnetic crystal with hexagonal-closed-packed symmetry on the direction of magnetization is generally expressed[45] by

$$E = K_0 + K_1\sin^2\theta + K_2\sin^4\theta + K_3\sin^6\theta + K_4\sin^6\theta\cdot\cos 6\phi + \cdots \tag{3.1}$$

where θ,ϕ are the angles that the magnetization makes with the hexagonal axis and one of the six axes directed towards neighbouring atoms in the basal plane, respectively. The anisotropy constants K_n are the quantities measured in anisotropy experiments.

A more convenient expansion for theoretical studies is in terms of Legendre polynomials[46]

$$E = K_0^0 + K_2^0P_2(\cos\theta) + K_4^0P_4(\cos\theta) + K_6^0P_6(\cos\theta) + K_6^6\sin^6\theta\cos 6\phi + \cdots \tag{3-2}$$

The K_n^m are known as anisotropy coefficients, $P_n(\cos\theta)$ is the n-th order Legendre polynomial. Both K_n and K_n^0 depend on temperature and external field, and in this investigation they are found to depend on pressure.

The anisotropy energy is obtained by torque measurement

experimentally, the torque exerted by a unit volume of specimen is

$$L = -\frac{dE}{d\theta} = A_2 \sin 2\theta + A_4 \sin 4\theta + A_6 \sin 6\theta \qquad (3\text{-}3)$$

where

$$\left.\begin{aligned} A_2 &= \frac{3}{2} K_2^0 + \frac{5}{8} K_4^0 + \frac{105}{256} K_6^0 \\ A_4 &= \frac{35}{16} K_4^0 + \frac{63}{64} K_6^0 \\ A_6 &= \frac{693}{256} K_6^0 \ . \end{aligned}\right\} \qquad (3\text{-}4)$$

Coefficients A_2, A_4 and A_6 in expression (3-3) are determined by Fourier analysis of the measured torque curves. Eq.(3-4) may be solved for K_2^0, K_4^0 and K_6^0 as follows:

$$\left.\begin{aligned} K_2^0 &= \frac{2}{3} A_2 - \frac{4}{21} A_4 - \frac{2}{63} A_6 \\ K_4^0 &= \frac{16}{35} A_4 - \frac{64}{385} A_6 \\ K_6^0 &= \frac{256}{693} A_6 \ . \end{aligned}\right\} \qquad (3\text{-}5)$$

3.2 Temperature Dependence of Magnetocrystalline Anisotropy of Gadolinium

The temperature dependence of the anisotropy constants of materials decreases with increasing temperature and generally become zero at Curie point, and which can be explained by a one-ion or pair model.

The temperature dependence [29),30)] of the anisotropy constants of Gd have two remarkable characteristics: that is, (i) K_2^0 (or K_1), which is dominant term in the anisotropy energy has a complicated temperature dependence, changing sign twice below Tc, (ii) **some part of the anisotropy energy is reserved above the Curie point(293°K) to about 360°K.**

Recently, the temperature dependence of the anisotropy of Gd was investigated theoretically by Brooks and Goodings [47)] using a localized spin model which includes a crystal field of hexagonal close-packed symmetry plus magnetic dipole-dipole interaction. The resulting agreement with the measurements for higher term K_2, K_3 in expression (3-1) is good, but the temperature dependence of main term K_1 is anomalous.

The one purpose of this paper is to study the origin on the complicated anosotropy K_1 (or K_2^0 in expression (3-2)). In Fig.(3.1), it is shown how the anisotropy constants change with temperature as obtained in this experiment.

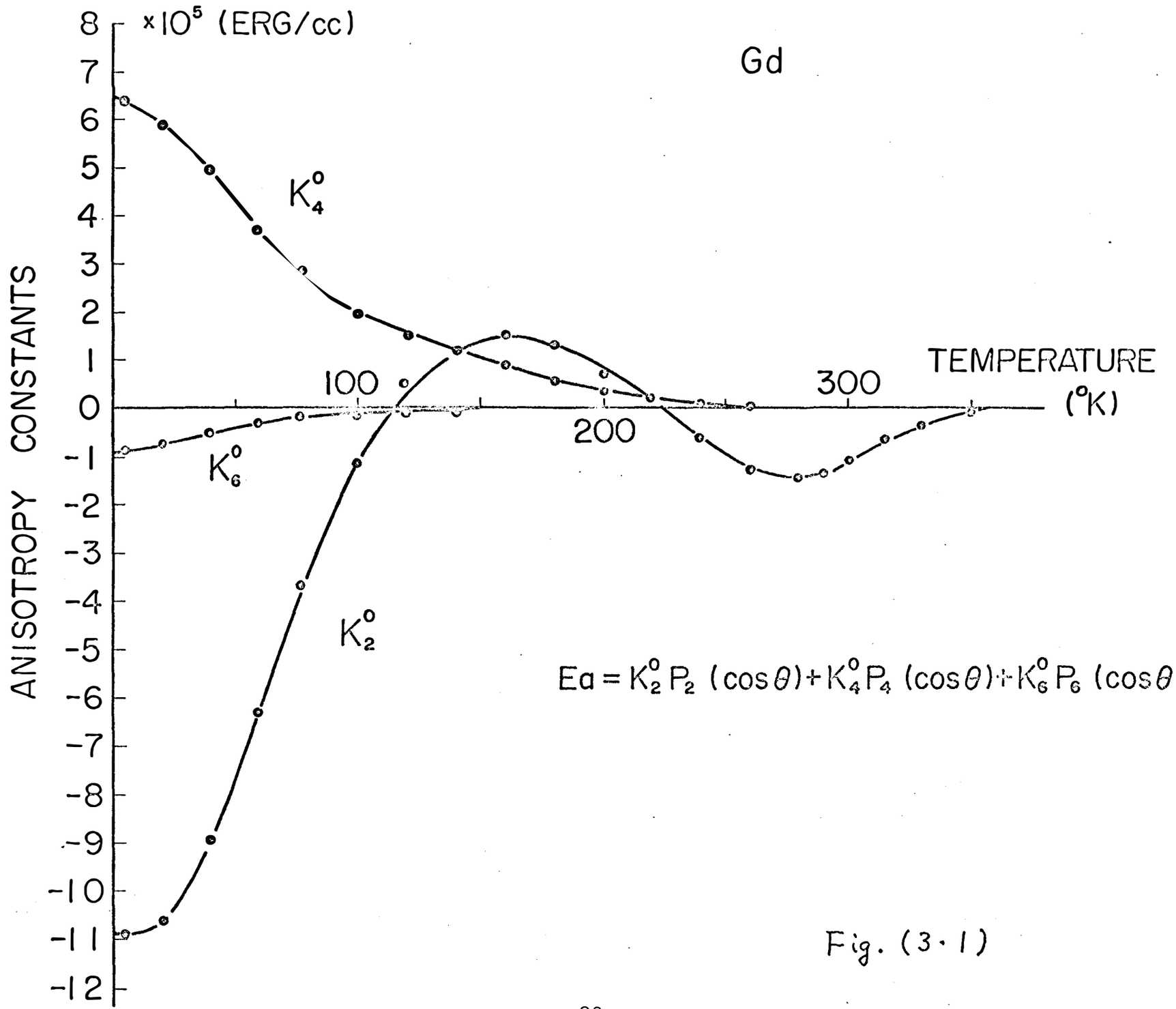
In this experiment, the torque is measured in the plane containing the hexagonal axis.

We believe that the experimental values of the anisotropy of Gd reported in the literature differ slightly by reason of sample purity and strains which grow in sample preparation. Especially, the latter will be most effective because the pressure depencence is larger than in other materials.

The magnetic anisotropy in basal-plane of Gd was measured by Graham[48] and others[49),50]. If the magnetization is confined to the (0001) plane, $\theta = \pi/2$ and the torque is given by

$$-\frac{dE}{d\theta} = 6\ K_4 \sin 6\phi\ .$$

He shows that the temperature dependence of K_4 follows approximately the 21st power of the magnetization. But, the magnitude of the anisotropy is very small because Gd has the easy axis in basal-plane.



$$Ea = K_2^0 P_2 (\cos\theta) + K_4^0 P_4 (\cos\theta) + K_6^0 P_6 (\cos\theta)$$

Fig. (3·1)

3.3. Saturation and Effective Moments of Gadolinium-Yttrium Alloys

(A) Saturation Moments of Gadolinium

The theory of ferromagnetism has been based on the spin exchange interaction between magnetic atoms or ions. Heisenberg's direct exchange interaction between nearest neighbors has been considered for the transition elements. The necessary condition for this interaction to take place is that the magnetic electrons of neighboring ions have overlapping orbits. Consequently, this model does not seem to apply to the magnetic rare-earth metals in which the magnetic shells of different ions have little or no overlap.

The ferromagnetism of rare earth metals is explained by RKKY interaction. This so-called indirect exchange interaction has been investrigated in detail by Ruderman and Kittel[51], Kasuya[52], and Yosida[53]. The 4f moments, being highly localized, polarize the conduction electrons via the inner field in the conduction bands. The experimentally determined value ($7.55\mu_B$)[54] of the saturation moment for gadolinium is significantly higher than the theoretical value ($7.00\mu_B$) obtained on the assumption of contributions by ionic spin only. The difference, $\Delta\mu$,

$$\Delta\mu = 0.55\ \mu_B \qquad (3\text{-}7)$$

is considered to be due to conduction electron polarization[55].

The exchange integral, J, was estimated Watson et al.[56]. They used an exchange Hamiltonian for the coupling between Bloch orbitals with wave vectors $\vec{k}$ and $\vec{k}'$. J is assumed to be a function of the scalar difference $|\vec{k} - \vec{k}'|$. The occurence of a ferromagnetic array of local moments induces an exchange splitting of the conduciton bands

$$\Delta_{ferro} = JSM \qquad (3\text{-}8)$$

where S is the expectation value of the local spin moment and M is temperature-dependent factor associated with the sublattice magnetization. J was estimated utilizing the conduction-electron moments $\Delta\mu$ observed in ferromagnetic gadolinium. Assuming no conduction-electron-conduction-electron enhancement of the respose, $\Delta\mu$ is given by

$$\Delta\mu = \frac{1}{4}\, g\, \mu_B\, N(E_F)\cdot\Delta_{ferro}. \qquad (3\text{-}9)$$

Taking $\Delta\mu=0.55\mu_B$ and the calculated value[57] of $N(E_F)=1.8$ electrons per atom per eV, Eqs.(3-8) and (3-9) yield

$$J \sim 0.087 \text{ eV}, \qquad (3\text{-}10)$$

assuming g=2 for the conduction electrons.

(B) Saturation Moments of Gadolinium-Yttrium Alloys

Although the saturation magnetization of Gd-Y alloys were measured already by Thoburn et al.[58], their experimental values scattered and we can not obtain the definite value of the saturation magnetization per Gd atom in Gd-Y alloys.

In the present work, the saturation magnetization on these alloys were measured up to 40 at. % Y. The magnetization was measured on a 6 mm diameter polycrystalline spherical samples at 4.2°K and 32 kOe using the integrated fluxmeter. The experimental results are shown Fig.(3.2). As shown in figure, the saturation moments per gram decrease with an increase of Y concentration in these alloy system. The addition of Y into Gd, however, increases the magnetic moment (μ_S) per Gd atom as shown in Fig.(3.3).

Then, it will discuss the cause that the magnetic moment per Gd atom increases with increasing the concentration of non-magnetic Yttrium. In Fig.(3.3), J can be estimated from the observed effective moments ($\mu_{eff}=g\mu_B\sqrt{J(J+1)}$) and we consider that 2J signifies the saturation magnetic moment per Gd in ferromagnetic state. (The effective moment will be described the next paragraph in detail.) In equation of (3-9), when Gd is diluted by Y, the g-factor, $N(E_F)$ and

Δ_{ferro} will be expected to change. With respect to the g-value, Popplewell et al.[60] showed that it doesn't depend on the concentration below 50 at. % Y. There were no experiment to make clear the change of $N(E_F)$ and Δ_{ferro}. Therefore, it is discussed on the experimental results using the simple model.

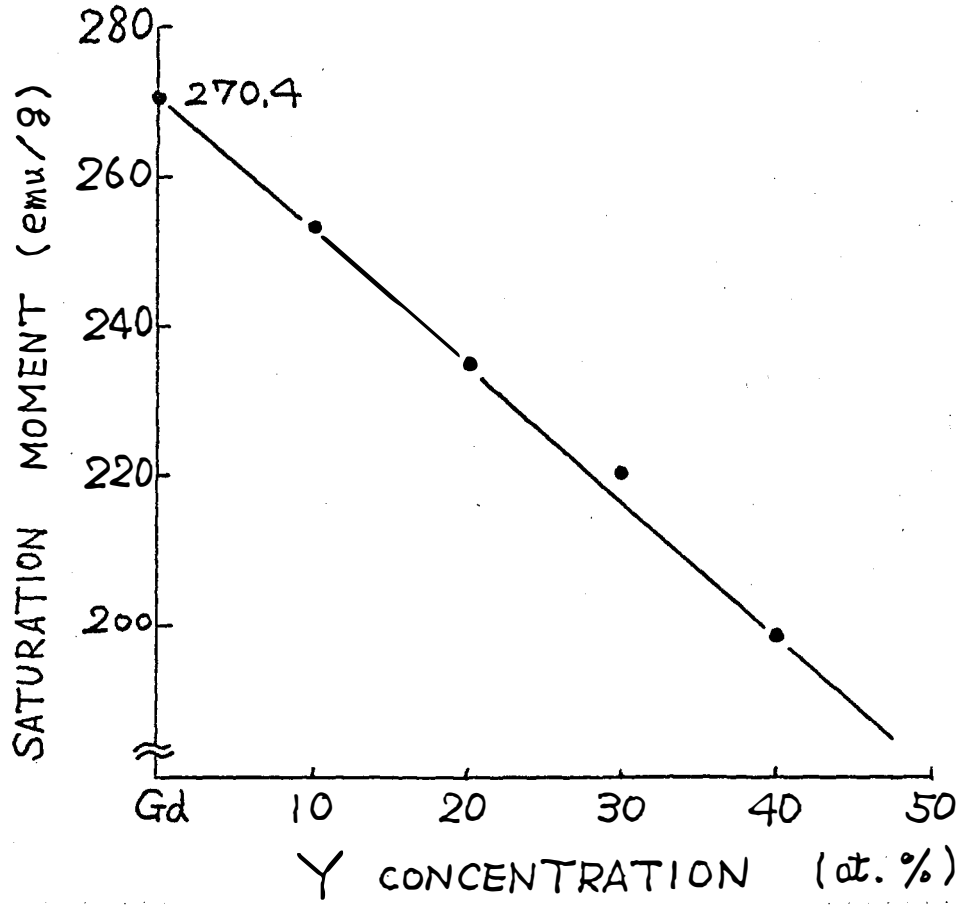


Fig.(3.2) : Saturation moment vs. Y concentrations in Gd-Y alloys.

The experimental saturation moment and the moment due to the theoretical value are defined as μ_s and μ_f(=7.00 μ_B) respectively. The magnetization due to the polarization of conduction electrons will be separated two parts : that is, (i) $\mu_{c.l.}$ is the temperature independent part of the polarized magnetic moment of conduction electrons by the 4f spin, (ii) $\mu_{c.c.}$ is the temperature dependent part of the polarized magnetic moment of conduction electrons. That is to say, μ_s can be written as follow,

$$\mu_s = \mu_f + \mu_{c.l.} + \mu_{c.c.} \quad . \qquad (3\text{-}11)$$

As shown in Fig.(3.3), μ_s, μ_f, $\mu_{c.l.}$ and $\mu_{c.c.}$ in pure Gd are estimated as follow : $\mu_{c.l.}$ = 0.40 μ_B, $\mu_{c.c.}$ = 0.15μ_B. Accordingly,

$$\mu_s = 7.00 + 0.40 + 0.15 = 7.55 \quad (\mu_B).$$

In region of high temperature, $\mu_{c.c.}$ is considered to be negligible small, so the moment per Gd atom is following

$$\mu_f + \mu_{c.l.} = 7.40 \ (\mu_B) \qquad (3\text{-}12)$$

The increase of the magnetic moment per Gd atom by addition of Y atoms may be ascribed to the contribution from conduction electrons. $\mu_{c.c.}$ is expected to be independent on the concentration of Y, because the μ_s and 2J are nearly parallel in Fig.(3.3). On the other hand, $\mu_{c.l.}$ increases with the contribution of Y and we obtain that the average magnetic polarization of Y atom is 0.20 μ_B from the linear concentration dependence of $\mu_{c.l.}$.

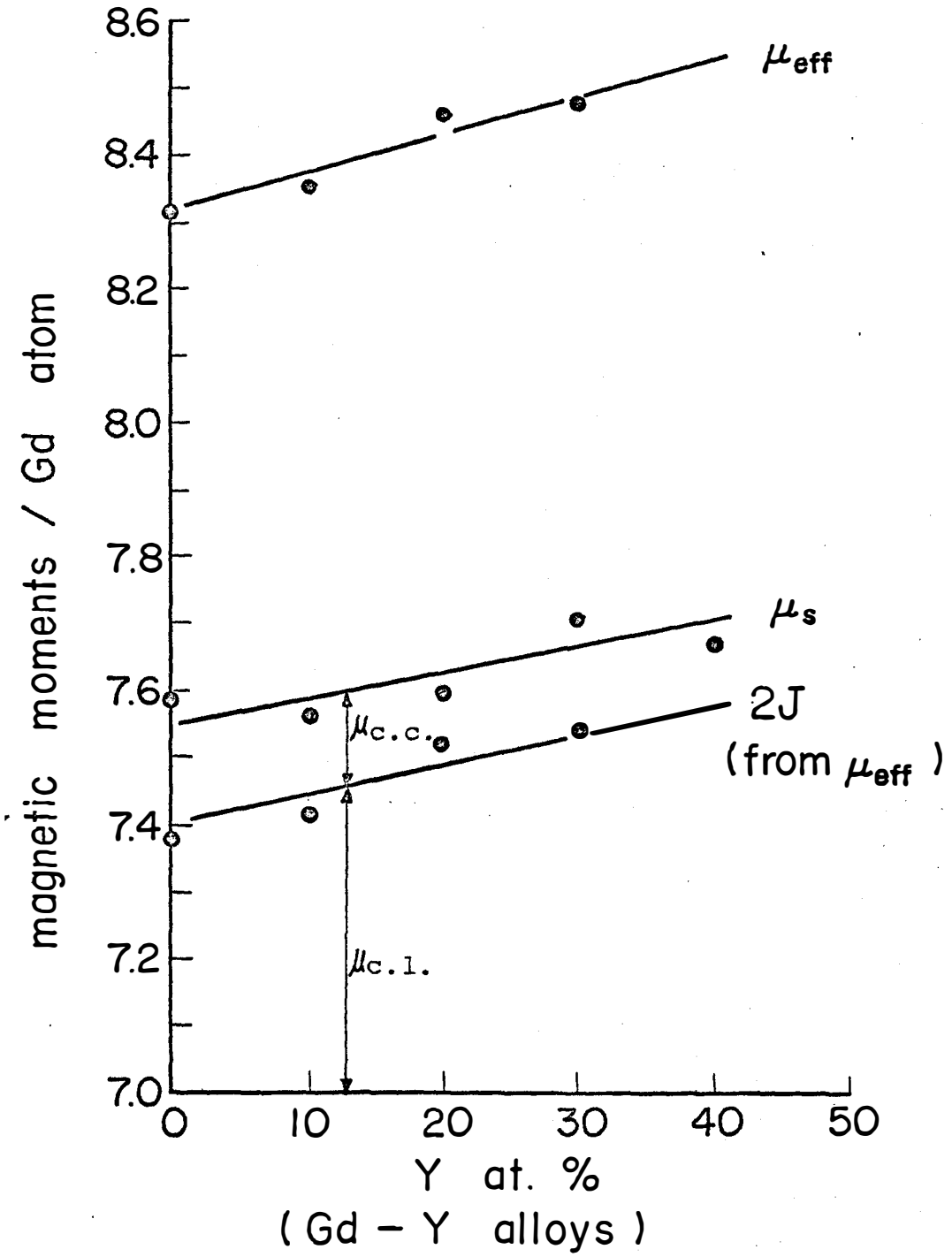
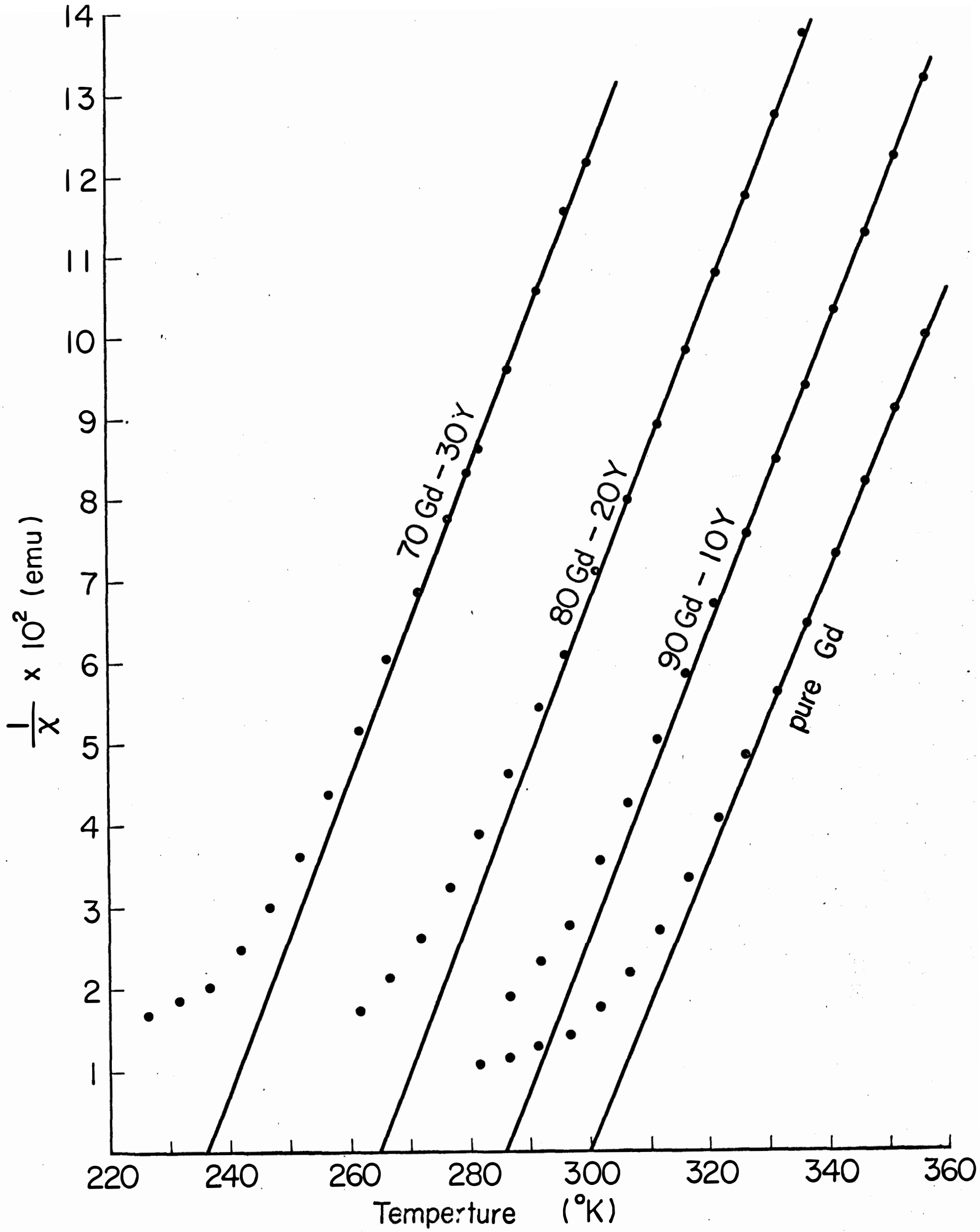

8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
magnetic moments / Gd atom
μ_{eff}
μ_s
2J
(from μ_{eff})
$\mu_{c.c.}$
$\mu_{c.l.}$
0
10
20
30
40
50
Y at. %
(Gd − Y alloys)

Fig. (3·3)



Inverse susceptbility as a function for Gd-Y alloys

Fig. (3·4)

(C) Effective Moment of Gadolinium-Yttrium Alloys

The effective moments of Gd-Y alloys were measured. They were obtained from the measurements of the temperature dependence of the magnetic susceptibility in the paramagnetic region.

Cylindrical polycrystalline samples, 0.7mm in diameter and 4.5mm in length, was used. For the measurements of the susceptibility, a pendulum type magnetometer was employed. The magnetic field was applied up to 10 kOe. Calibration was done using Mn-tutton salts.

The effective moments μ_{eff} ($=g_J\mu_B\sqrt{J(J+1)}$) were determined from slop of ($\frac{1}{\chi}$ - T) curve in the high temperature linear region by applying the Curie-Weiss law, $\chi = C/(T-\theta)$, where θ is the paramagnetic Curie temperature and C is given by

$$C = \frac{N\, g_J^{\,2}\, \mu_B^{\,2}\, J\,(J+1)}{3k} . \qquad (3\text{-}13)$$

In Eq.(3-13), N is the number of atoms per unit weight (3.83×10^{21} per gram for Gd), g_J is the Lande's g-factor (2 for Gd), J is the total angular momentum (J=7/2 for Gd), and k is Boltzmann constant.

Inverse susceptibility ($1/\chi$) vs. temperature (T) curves are shown in Fig.(3.4). From Fig.(3.4), the value of C for

Gd was obtained as 55.1×10^{-3} deg/(emu/g), so that $\mu_{eff}=8.32\ \mu_B$.

In previous literatures, the experimental[61] and the theoretical values are about the same, 7.93 μ_B and 7.94 μ_B, respectively. Elliot[61] got 7.12 μ_B as the value of the saturation magnetization which is also close to the theoretical value 7 μ_B. However, in present time, all reliable experimental results are also to $\mu_S=7.55\ \mu_B$. We think that the Elliot's samples were bad in purity. And the value of the effective moment is not so reliable as our results.

The value of the present work, 8.32 μ_B, differs from the theoretical value of 7.94 μ_B by 0.38 μ_B, which is smaller than the difference (0.55μ_B) between experimental and theoretical value for the saturation moment. The value 0.17μ_B (=0.55μ_B -0.38μ_B) will correspond to $\mu_{c.c.}$ in Eqs.(3-11).

For Gd-Y alloys, the Curie constants C and the paramagnetic Curie points θ_p obtained from ($\frac{1}{\chi}$ - T) curves in Fig.(3.14) are shown in Table (3-A)

Table (3-A)

	pure Gd	90Gd-10Y	80Gd-20Y	70Gd-30Y
C	55.0×10^{-3}	52.3×10^{-3}	49.9×10^{-3}	46.0×10^{-3}
θ_p (°K)	300	286	264.8	236

The effective moment μ_{eff} per one Gd atom is shown in Fig.(3.3) for Gd-Y alloys. The introduction of Y into Gd increases the effective moment per Gd. To compare the effective moment with the saturation moment, the total angular momentum J was deduced from μ_{eff}. The values of 2J (g=2 for g μ_B J) per one Gd atom are shown in Fig.(3.3).

Discussion about the values of 2J was given in the preceding paragraph.

3.4. Temperature Dependence of Magnetocrystalline Anisotropy of Gadolinium-Yttrium Alloys

As shown in Fig.(3.1), pure Gd metal exihibits a relatively small anisotropy, which, however rather complicated temperature dependence.

The temperature dependence of the anisotropy of Gd-Y alloys was measured to investigate the origin of this complicated anisotropy of Gd.[62] The reason that Y was chosen as the diluting material is that it has almost the same crystal structure (h.c.p.), lattice parameter, atomic volume, electronic state (valency +3) as Gd, so that the introduction of Y increases the average Gd- Gd distance and gives a certain effect on the atomic interactions between Gd atoms.

It is repoted[58] that the Gd-Y alloys exibit ferromagnetic within and anti-ferromagnetic without 40 at. % Y.

In this work, the four single crystals were prepared, that is, 10. 20, 30 at. % Y and pure Gd. The torque was measured in the plane containing the hexagonal axis using the field of 31 kOe. The anisotropy constants of Gd-Y alloys were determined by Fourier analysis of the measured torque curve and are plotted against temperature in Fig. (3.5), (3.6) and (3.7).

As shown in figures, it is found that the addition of non-magnetic constituent Y causes a drastic change in the anisotropy of Gd-Y alloys. The anisotropy constant K_2^0 of 30 at. % Y is larger than the value for pure Gd at 0°K. Consequently, it appears that simple models such as the one-ion or pair model can not completely explain the anisotropy of Gd. Because, their models should reduce the magnetization and the anisotropy energy of the alloys. The K_4^0 term decreases linearly with the increasing of Y contents. It will be in proportion to the decrease of the magnetization. The K_6^0 term changes with Y contents. However, it can not discuss, since the order is a smaller than K_2^0.

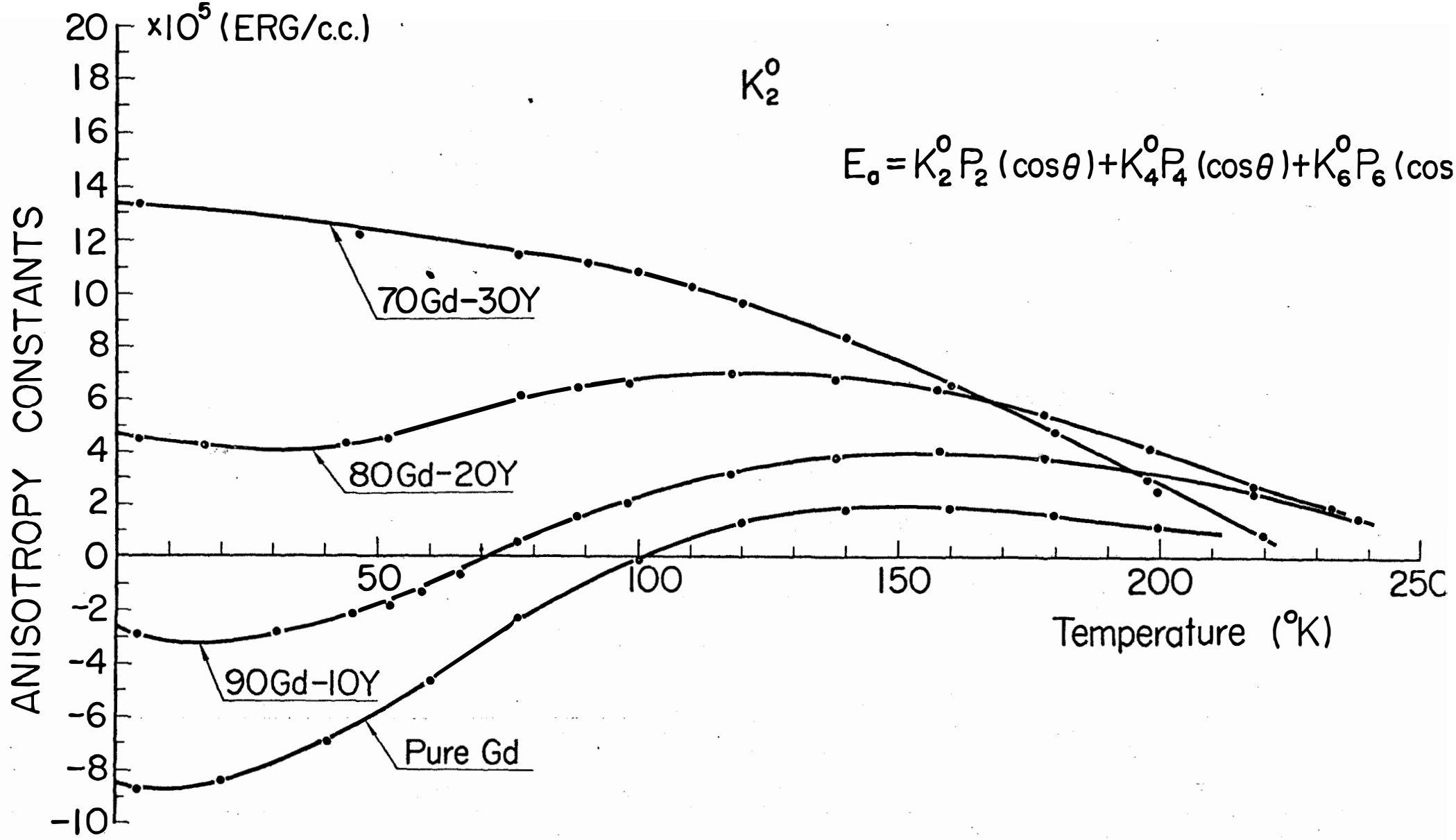


Fig. (3.5) Temperature dependence of the anisotropy constants of Gd−Y alloys

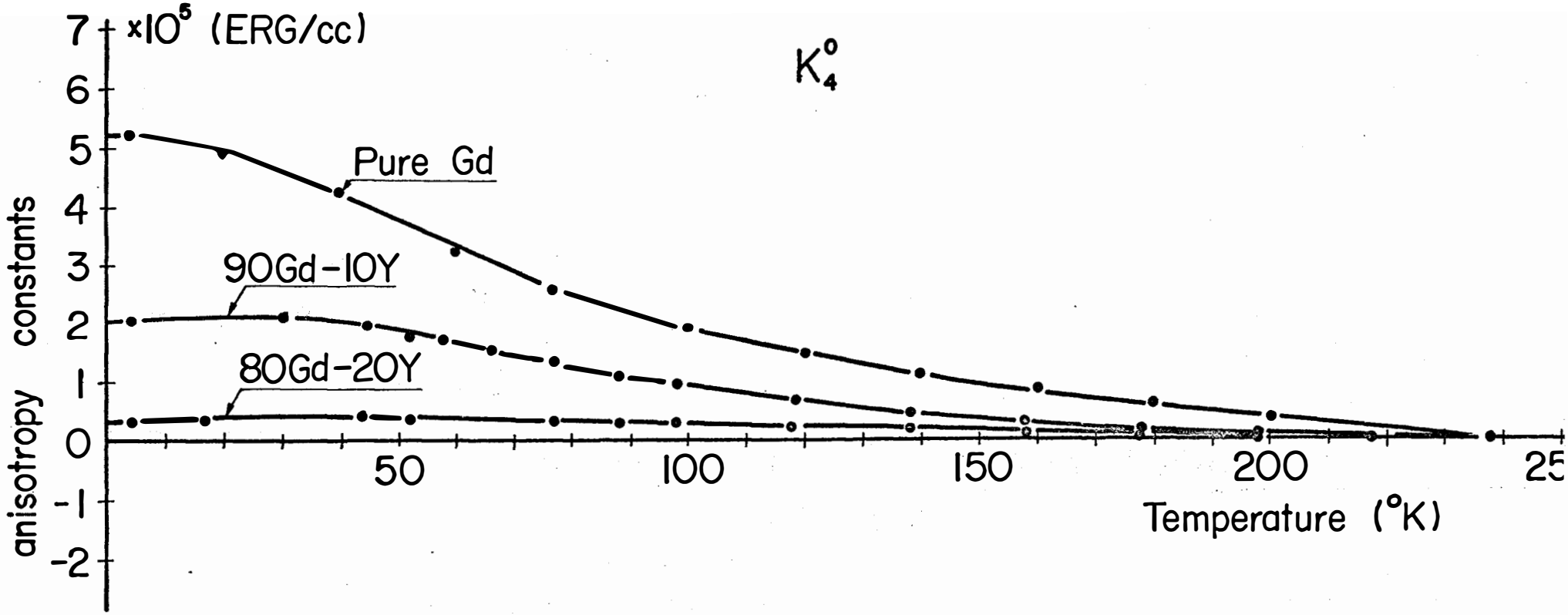

×10^5 (ERG/cc)
K_4^0
Pure Gd
90Gd-10Y
80Gd-20Y
anisotropy constants
7
6
5
4
3
2
1
0
-1
-2
50
100
150
200
25
Temperature (°K)

Fig. (3·6)

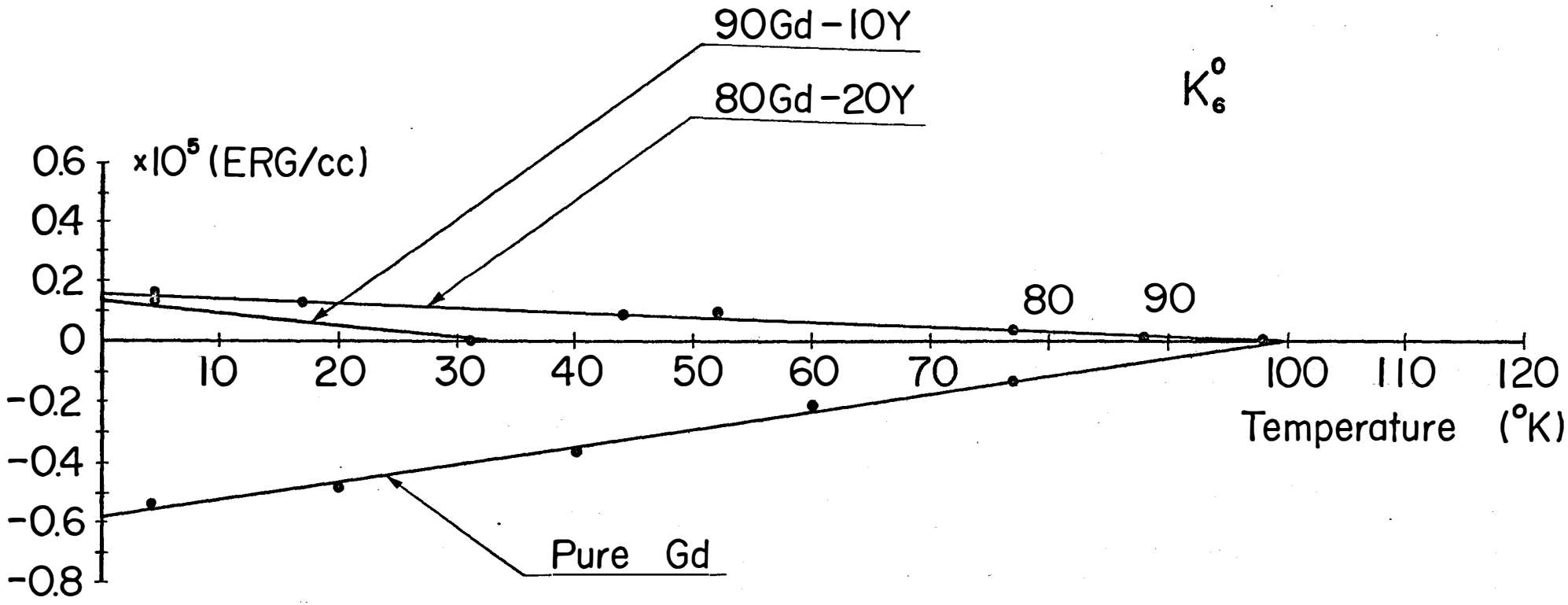

90Gd-10Y
80Gd-20Y
K_6^0
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
x10^5 (ERG/cc)
10
20
30
40
50
60
70
80
90
100
110
120
Temperature (°K)
Pure Gd

Fig. (3·7)

3.5. Pressure Dependence of Magnetocrystalline Anisotropy of Gadolinium

(A) Pressure Dependence at 77°K

Measurement was made by means of a torque magnetometer[36] by rotating the magnetization in a plane containing the c-axis with an applied magnetic field of 31 kOe at 77°K under hydrostatic pressure up to 4.4 kbar. The single crystal of Gd, 4.5 mm in diameter and 1.45 mm in thick, was used. The specimen was inserted into a small Cu-Be clamped type high pressure bomb[38] which was set on the torque magnetometer.

The anisotropy constants were determined by Fourier analysis of the measured torque curves and are plotted against pressure by a solid line in Fig.(3.8).[62~64] The pressure dependence in this case is fairly large as compared with those for other materials such as Fe, Ni and ferrites which are of the order of a few per cent at 5 kbar.[65,66] Also, Fig.(3.8) shows by a broken line the temperature dependence of the anisotropy constants measured for the same specimen in the temperature range from 77°K to 120°K under the atmospheric pressure. It is interesting to note that the pressure dependence of the these constants are quite similar to their temperature dependence.

The reason of the similarity between pressure-and temperature-dependences is considered that some factor which governs the magnetocrystalline anisotropy, such as the lattice constant, spontaneous magnetization, or electronic structure is similarly changed by pressure and temperature.

Table (3-B)

	TEMPERATURE 77 ⟶ 120 (°K)	PRESSURE 0 ⟶ 4.4 (kbar)
μ_s	− 6.5 (%)	− 0.46 (%)
a	+ 0.02	− 0.45
c	− 0.01	− 0.09
c/a	− 0.03	+ 0.36

μ_s : saturation magnetization

a, c : lattice constant

First of all, as shown in Table (3-B), saturation magnetization decreases with increasing temperature, and also decreases with increasing pressure.[48,70] The fractional change is, however, about 6∿7 % for temperature dependences from 77°K to 120°K, while 0.46 % for pressure dependence. The value of a and c/a are not responsible for the anisotropy change, since the magnitude is too small and also the sign is different between pressure[68,69] and temperature dependences.[67] The value of c is reduced by pressure and temperature, but the magnitude differs.

Therefore, the saturation magnetization or the lattice constants is excluded as the direct origin of the anisotropy change.

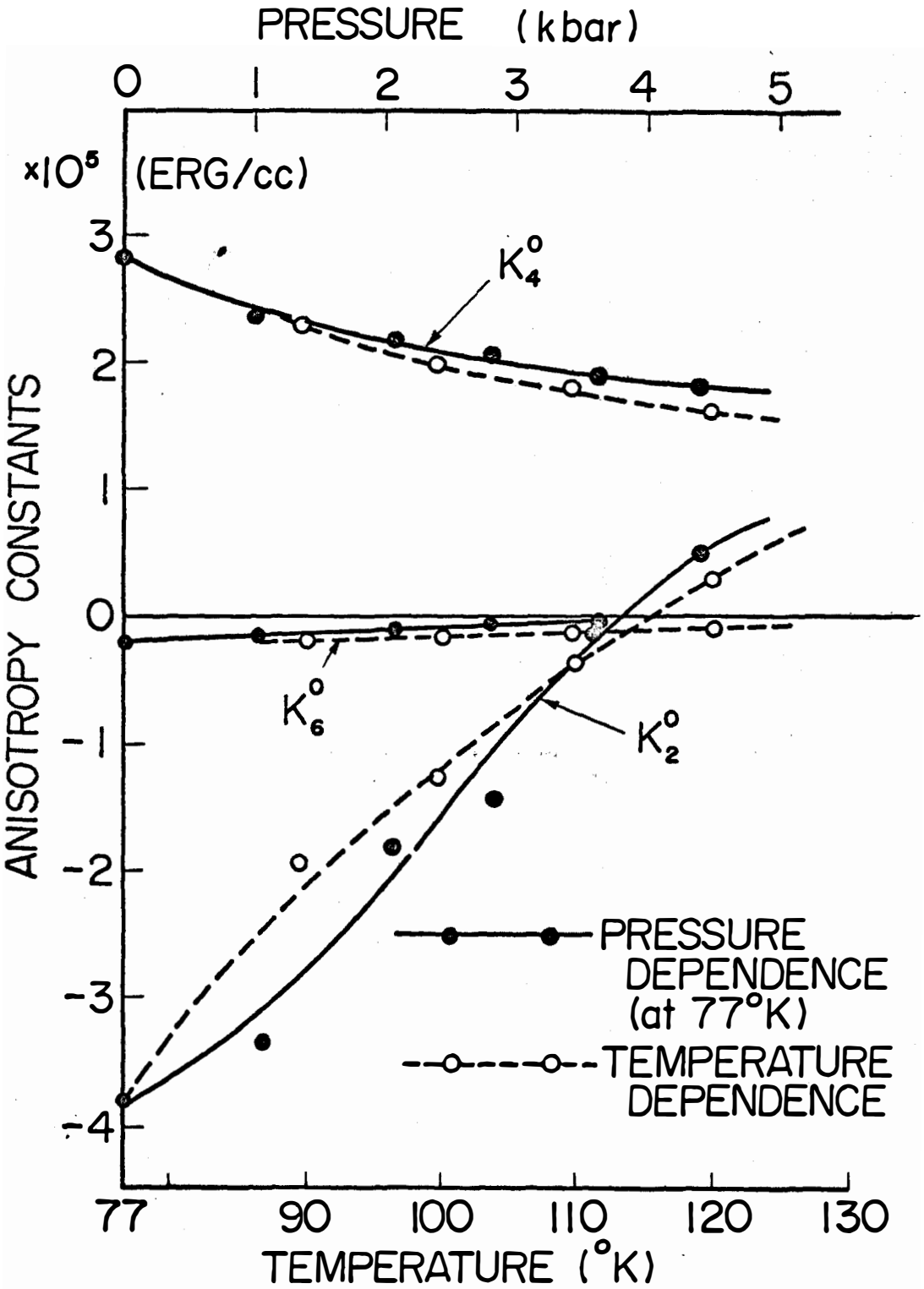

PRESSURE (kbar)
0
1
2
3
4
5
×10⁵ (ERG/cc)
3
2
1
0
-1
-2
-3
-4
ANISOTROPY CONSTANTS
K_4^0
K_6^0
K_2^0
PRESSURE DEPENDENCE (at 77°K)
TEMPERATURE DEPENDENCE
77
90
100
110
120
130
TEMPERATURE (°K)

Fig. (3.8)

(B) Temperature Dependence on the Anisotropy under the High Pressure

The temperature dependence of the anisotropy constant K_2^o of Gd has a remarkable characteristic. The value of K_2^o is very large even at the Curie temperature and is observed above the Curie point (293°K) up to about 360°K.

The pressure-and temperature-dependencies of the anisotropy of Gd were measured at the Curie point (293°K). These results are shown in Fig. (3.9) and (3.10). The pressure dependence of the anisotropy constants of Gd at 77°K is similar to the temperature dependence, but it is quite different at the Curie temperature as shown in Fig. (3.1) and (3.9). The anisotropy constant K_2^o increases with the increase of the applied hydrostatic pressure, and decreases with the increase of the temperature. The field dependence of the anisotropy was also measured for the same specimen in the field range from 5 kOe to 31 kOe under 0 kbar and 4.85 kbar. The results are shown in Fig. (3.10). The field dependence under 4.85 kbar do not saturate up to 31 kOe. The Curie point of Gd is 286°K under the 4.85 kbar[68,71~78]. Therefore, the 4.85 kbar is in a paramagnetic region.

The magnetic anisotropy energy originates from the

tendency that the orientation of the spontaneous magnetic moment along some directions in crystal is energetically more favourable than along other directions. Therefore, if the spontaneous magnetic moment vanishes, the anisotropy also disappears. Thus the anisotropy, observed in this experiment at the Curie temperature, must be induced by the external magnetic field.

In the high temperature region above the Curie point, the moment per Gd atom is $7.40\mu_B$. Of this value $7.40\mu_B$, the $0.40\ \mu_B$ will be the contribution due to the polalization of the magnetic conduction electrons by the 4f spin. Accordingly, the changes of the anisotropy under high pressure at 293°K may be ascribed to the contribution from conduction electrons.

Next, the temperature dependence of the anisotropy under hydrostatic pressure was measured in the temperature region from 77°K to 293°K. The correction of pressure within high pressure bomb was made using the calibration curve shown in Fig. (2.5). For the measurement of the three temperature points, the freezing mixture was used as

77°K : liquid nitrogen.

201°K: dry ice plus ethyl alcohol.

273°K: ice plus water.

The measurement was done for the several pressure points at the each temperature. The pressure dependence of the anisotropy constant at the characteristic temperature points is shown in Fig. (3·12), (3·13) and (3·14) . Fig. (3·11) shows the temperature dependences of the anisotropy constant K_2^o under the hydrostatic pressure 3 and 5 kbar. The anisotropy changes with the pressures complicatedly. At 77°K, the sign of the anisotropy constant change from negative to positive with the increase of the applied pressure. From the observation, we first supposed that the whole curve of the temperature dependence of the anisotropy constant would shift to positive value. However measurement near the Curie point revealed the negative shift of the torque curve. At the Curie temperature the absolute value of the anisotropy constant increases with negative sign. It is noticeable that the pressure dependence of the anisotropy constant is large compared with the pressure dependence of the Curie temperature. (The change is very small at 3 and 5 kbar as shown by arrows.) The anisotropy constant has local maxima at about 150°K and 270°K. This phenomena will not be essential because these maxima would dissappear with the increase of the applied pressure. However, in this process, the practical limitation exists. The crystal makes a transformation.

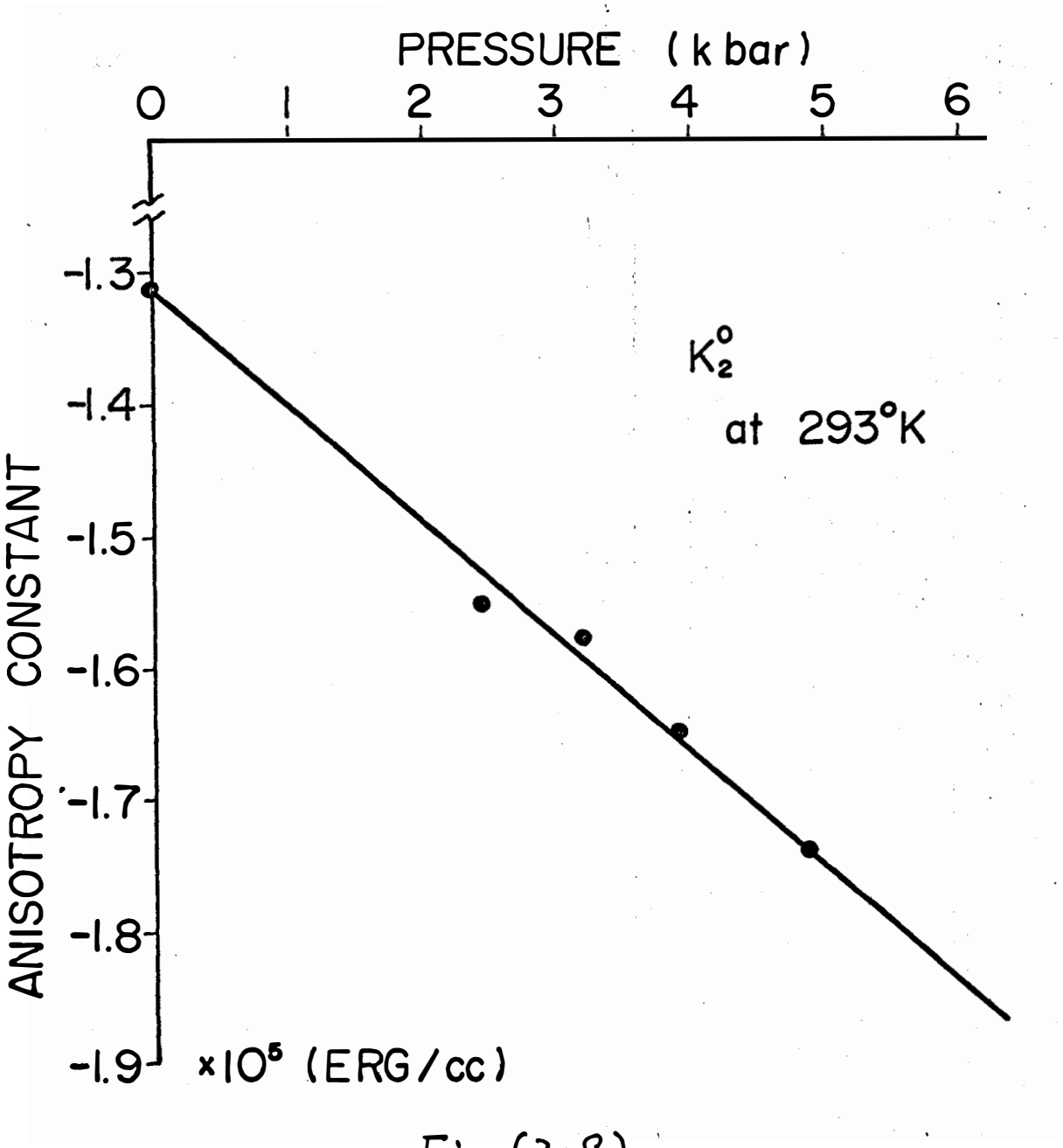

PRESSURE (k bar)
0
1
2
3
4
5
6
-1.3
-1.4
-1.5
-1.6
-1.7
-1.8
-1.9
ANISOTROPY CONSTANT
×10⁵ (ERG/cc)
K₂⁰
at 293°K

Fig. (3·9)

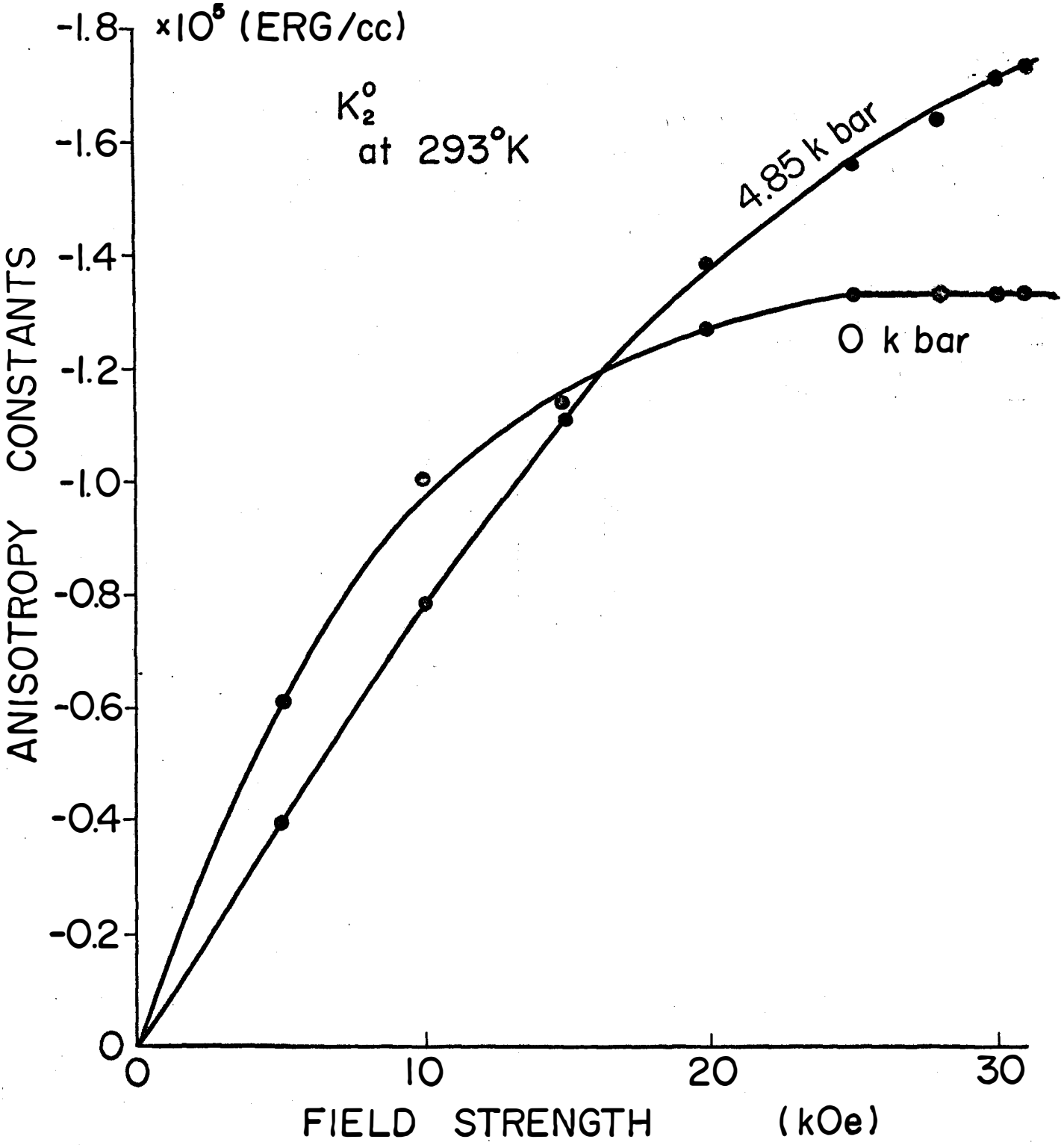

-1.8
×10⁵ (ERG/cc)
K_2^0
at 293°K
-1.6
4.85 k bar
-1.4
0 k bar
-1.2
-1.0
-0.8
-0.6
-0.4
-0.2
0
ANISOTROPY CONSTANTS
0
10
20
30
FIELD STRENGTH (kOe)

Fig. (3·10)

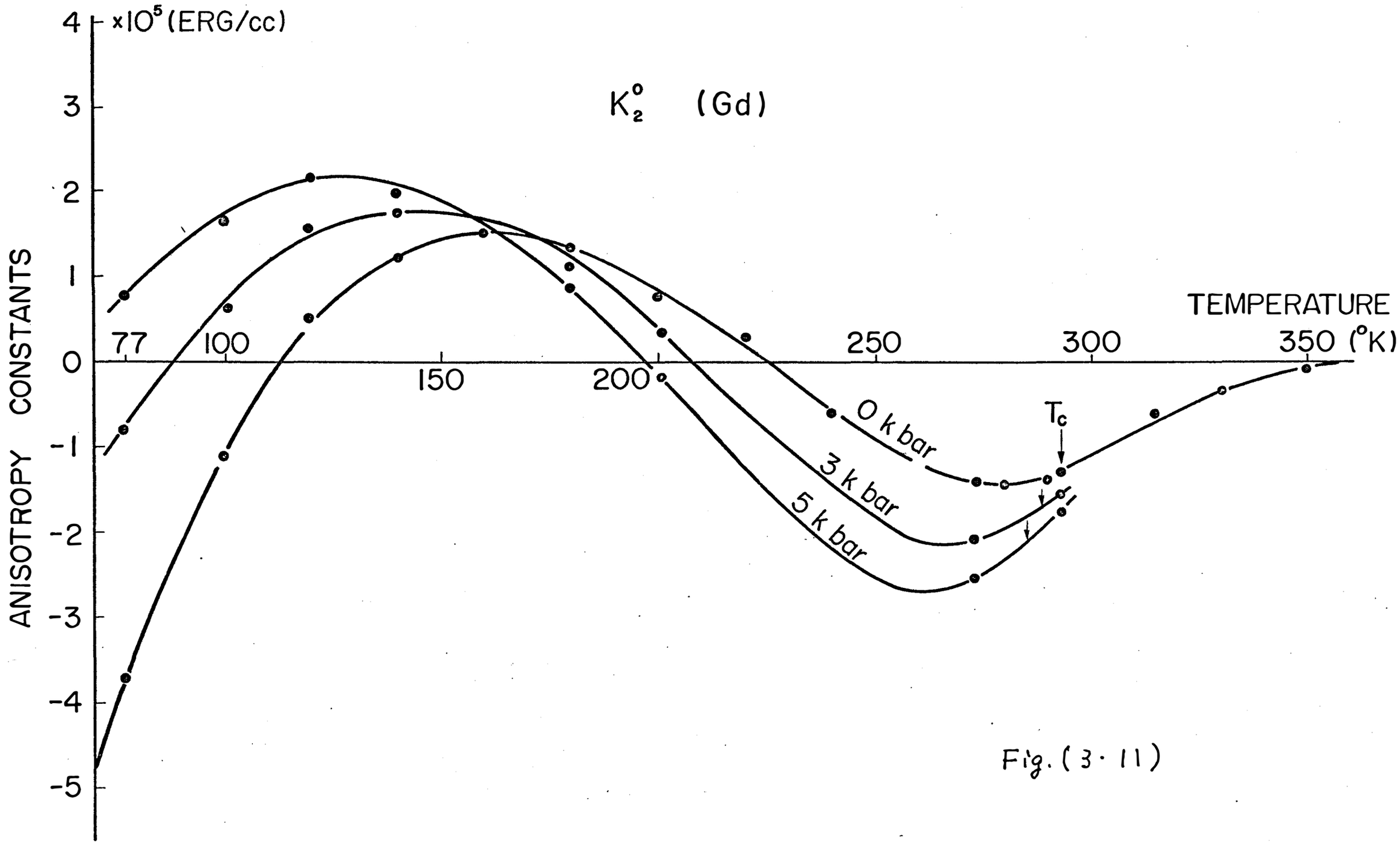

×10⁵ (ERG/cc)
4
3
2
1
0
-1
-2
-3
-4
-5
ANISOTROPY CONSTANTS
K_2^0 (Gd)
TEMPERATURE
77
100
150
200
250
300
350 (°K)
0 k bar
3 k bar
5 k bar
T_c

Fig. (3·11)

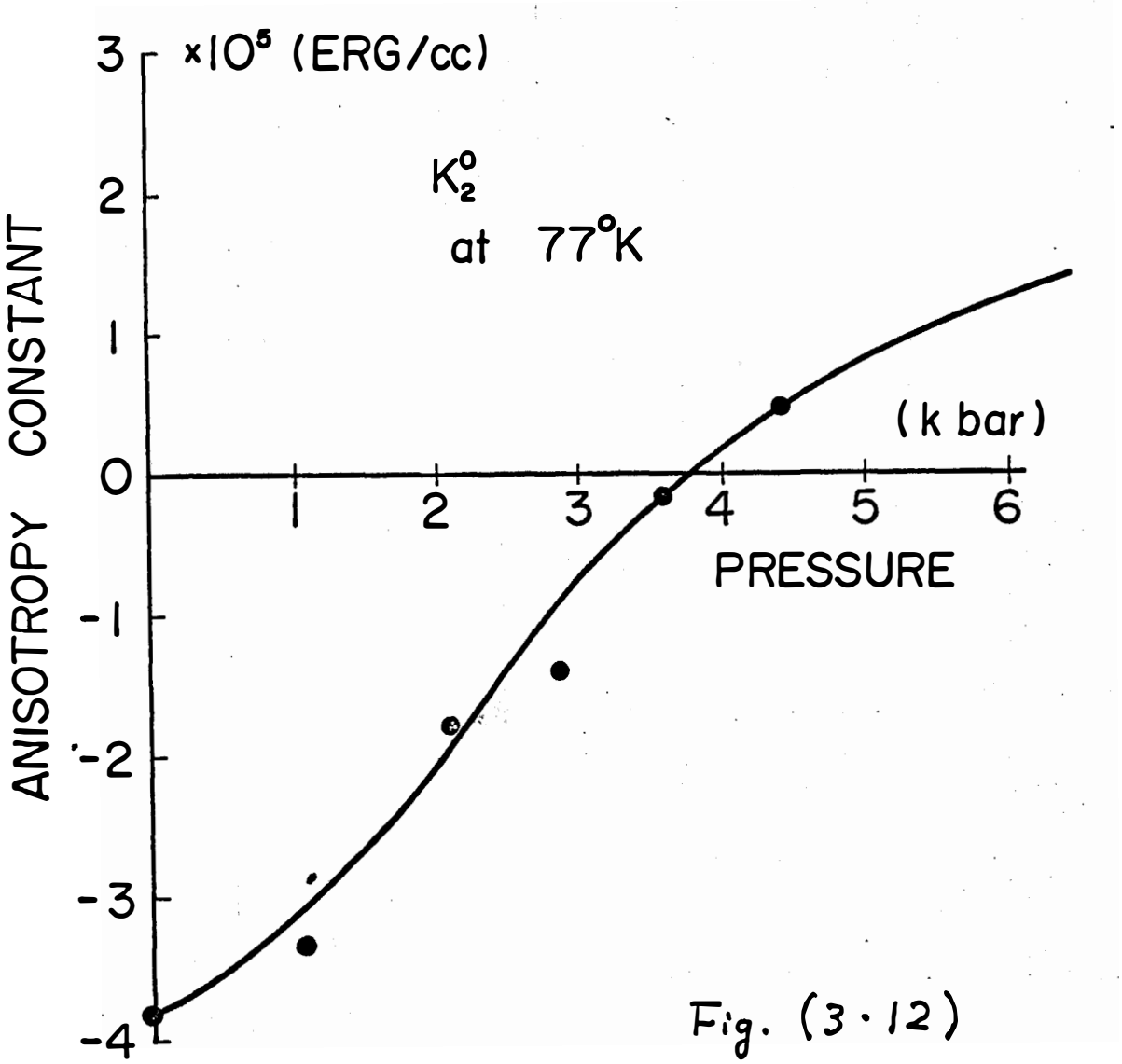

×10⁵ (ERG/cc)
ANISOTROPY CONSTANT
K_2^0
at 77°K
(k bar)
PRESSURE
3
2
1
0
-1
-2
-3
-4
1
2
3
4
5
6

Fig. (3·12)

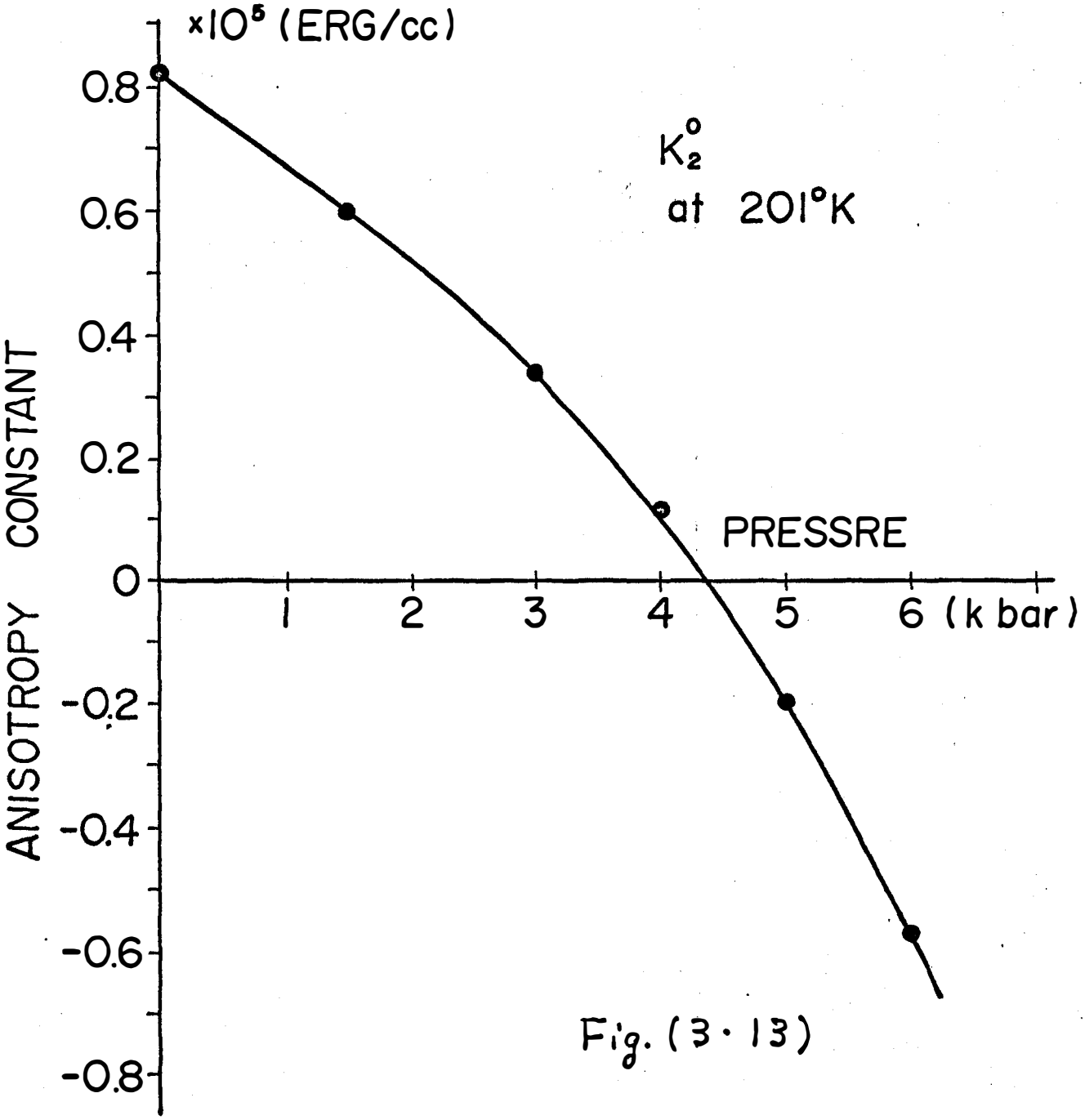

×10⁵ (ERG/cc)
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
ANISOTROPY CONSTANT
K_2^0
at 201°K
PRESSRE
1
2
3
4
5
6 (k bar)

Fig. (3·13)

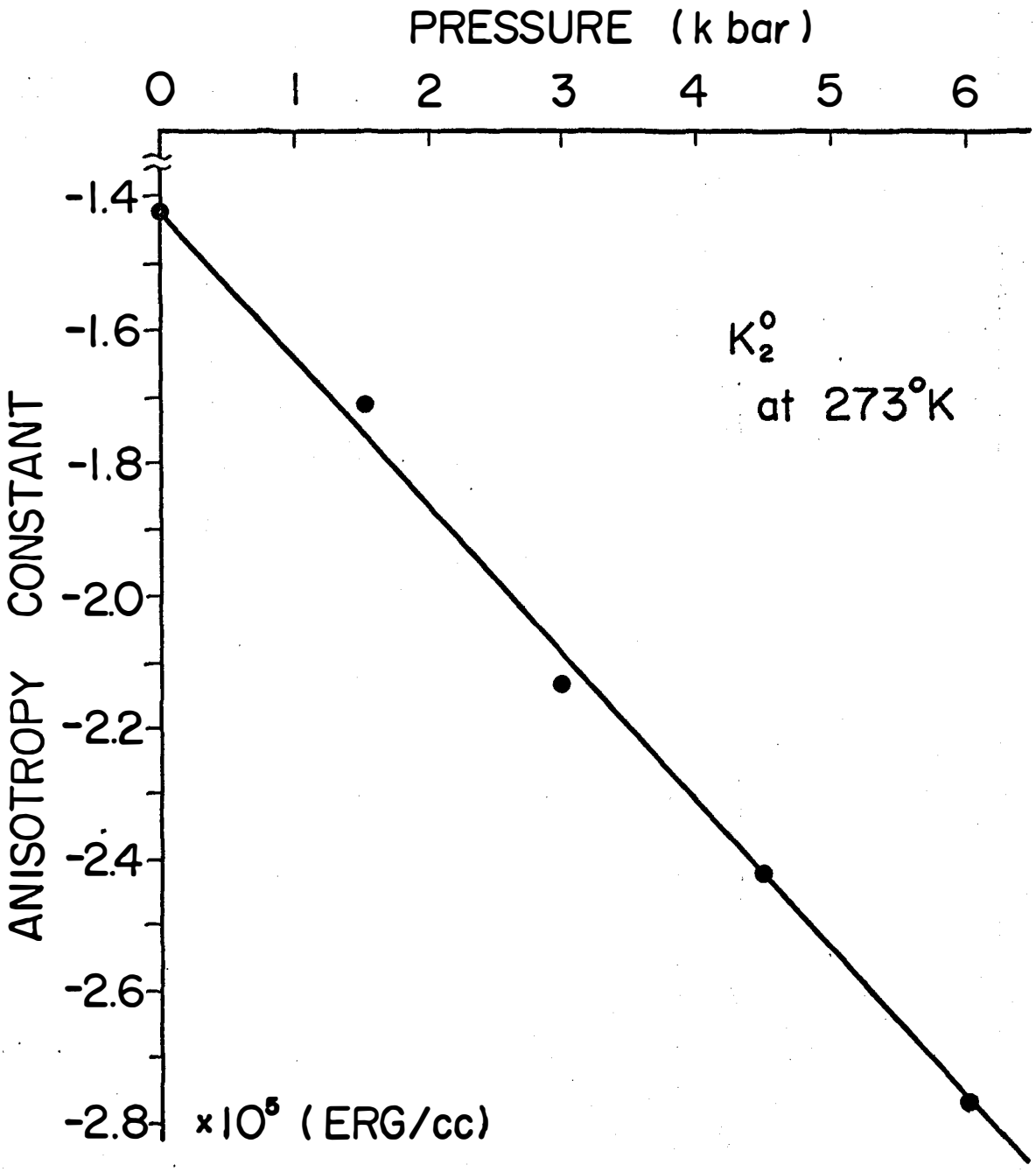

PRESSURE (k bar)
0
1
2
3
4
5
6
-1.4
-1.6
-1.8
-2.0
-2.2
-2.4
-2.6
-2.8
ANISOTROPY CONSTANT
K_2^0
at 273°K
×10⁵ (ERG/cc)

Fig. (3·14)

Chapter 4. DISCUSSION

4.1. Properties of Gadolinium and Yttrium

(A) Properties of Gadolinium

The crystal structure of Gd is hexagonal close-packed and the lattice constants are a = 3.6315 Å, c = 5.777 Å and c/a = 1.5908. Heavy rare earth metals have the same structure. The Curie Temperature of the ferromagnetic ordering is 293°K. Only a simple ferromagnetic ordering is ovserved below the Curie Temperature and other complex structures such as screw spin state are not realized.

In Gd metal, the Gd atom is in the ionic state Gd^{3+}. The unfilled shell of the 4f electrons are weakly affected by their environment, because the ion has an outer filled shell of $(5s)^2(5p)^6$ electrons.
As a result the direct exchange interaction between the 4f electron spin of a atom and the 4f electrons of the neighbouring atoms are negligibly small, the most important exchange interaction is the indirect exchange interaction between the 4f electron spins via the conduction band of $(5d)^1(6s)^2$ electrons. The ground state of Gd^{3+} ion is $^8S_{7/2}$.

The anisotropy energy of Gd is the order of 10^6 erg/cc. This value is very small compared with other rare earth metals($\sim 10^8$ erg/cc), but is not small compared with 3d transition metals such as Fe($\sim 10^5$ erg/cc), Co($\sim 10^6$erg/cc) or Ni($\sim 10^4$erg/cc).

The magnetic properties of conduction electron in pure Gd will be related to the band structure. The band structure was calculated by Dimmock and Freeman[57] using a non-relativistic augmented plane wave[79] (APW) method. The result is shown in Fig.(4.1).

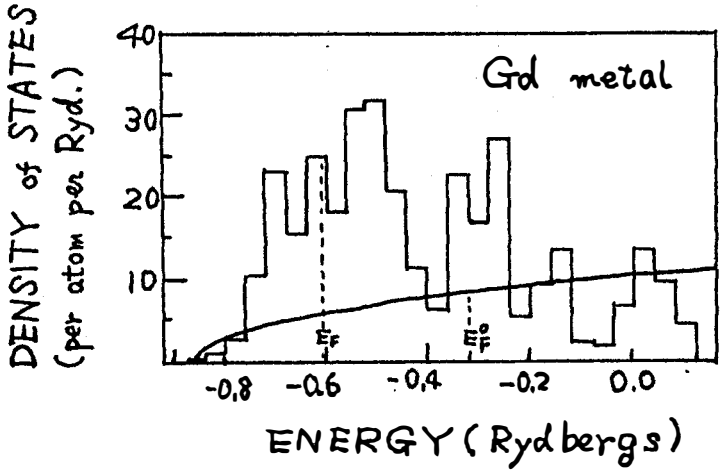


Fig.(4.1); A histogram representation of the density of states in electrons per atom per Ryd. The parabolic curve is the prediction of the free electron model. (refer to 57)

From Fig.(4.1) the density of states of Gd is obtained as 1.8 eV^{-1}. This value is about three times larger than that obtained using a free electron model.

(B) Properties of Yttrium

The crystal structure of Yttrium(Y) is hexagonal close-packed as Gd and the lattice constants are a = 3.6474 Å, c = 5.7306 Å and c/a = 1.5711. In Y metal, the Y atom is in the ionic state Y^{+3}. The Y^{+3} ion has an electron structure of $(3d)^{10}(4s)^2(4p)^6$ and contributes to the valence band its $(4d)^1(5s)^2$ electrons. Y is a non-magnetic metal itself. It has a susceptibility $\chi=1.8\times10^{-6}$(emu/g) and exhibits Pauli paramagnetism.

Y is the trivalent forth-period element which has the same crystal structure as gadolinium and nearly the same atomic volume. In an alloy,it will increase the average distance between the gadolinium atoms and hence affect the interaction between them. The band structure was calculated by using A.P.W. method by Loucks[80]. The density-of-states curve of Y is shown in Fig.(4.2). At the Fermi energy the density of states is 26.8 electrons/atoms Ry.(= about 1.8 eV^{-1}) and the value is similar to gadolinium metal.

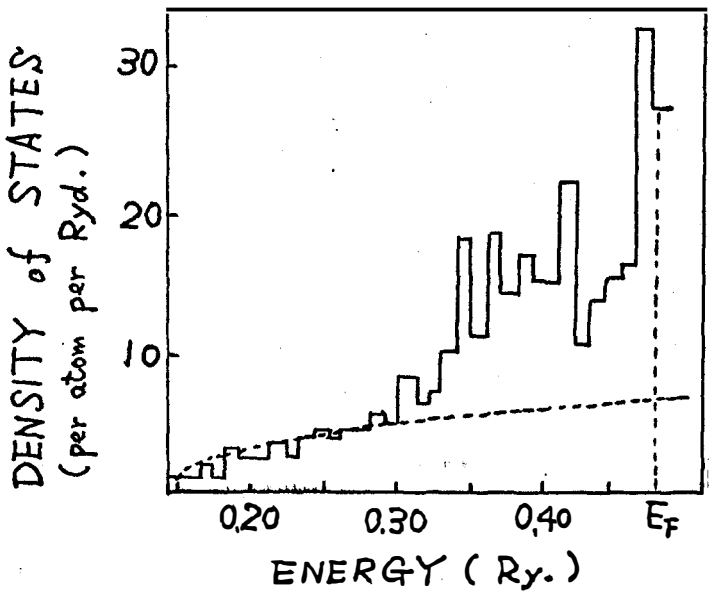


Fig.(4.2); Density of States curve for Yttrium. Solid line is the APW result, and the broken line is from the free electron model. (refer to 80)

The temperature and pressure dependence of lattice constants of pure gadolinium are reviewed in Fig.(4.3),(4.4),(4.5) and (4.6).

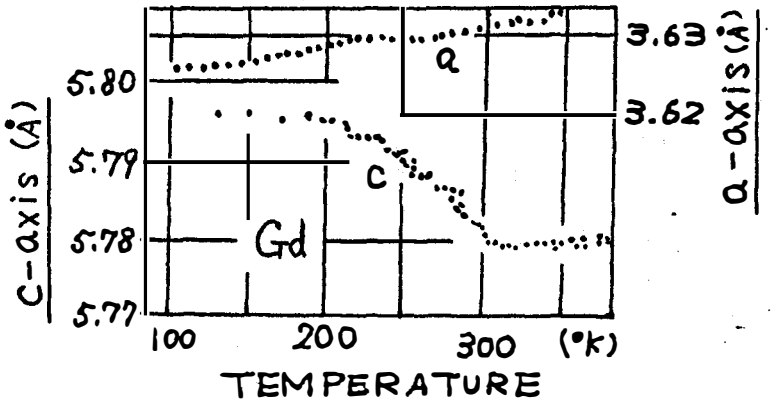


Fig.(4.3); Temperature dependence of the lattice constants of pure gadolinium (refer to 67)

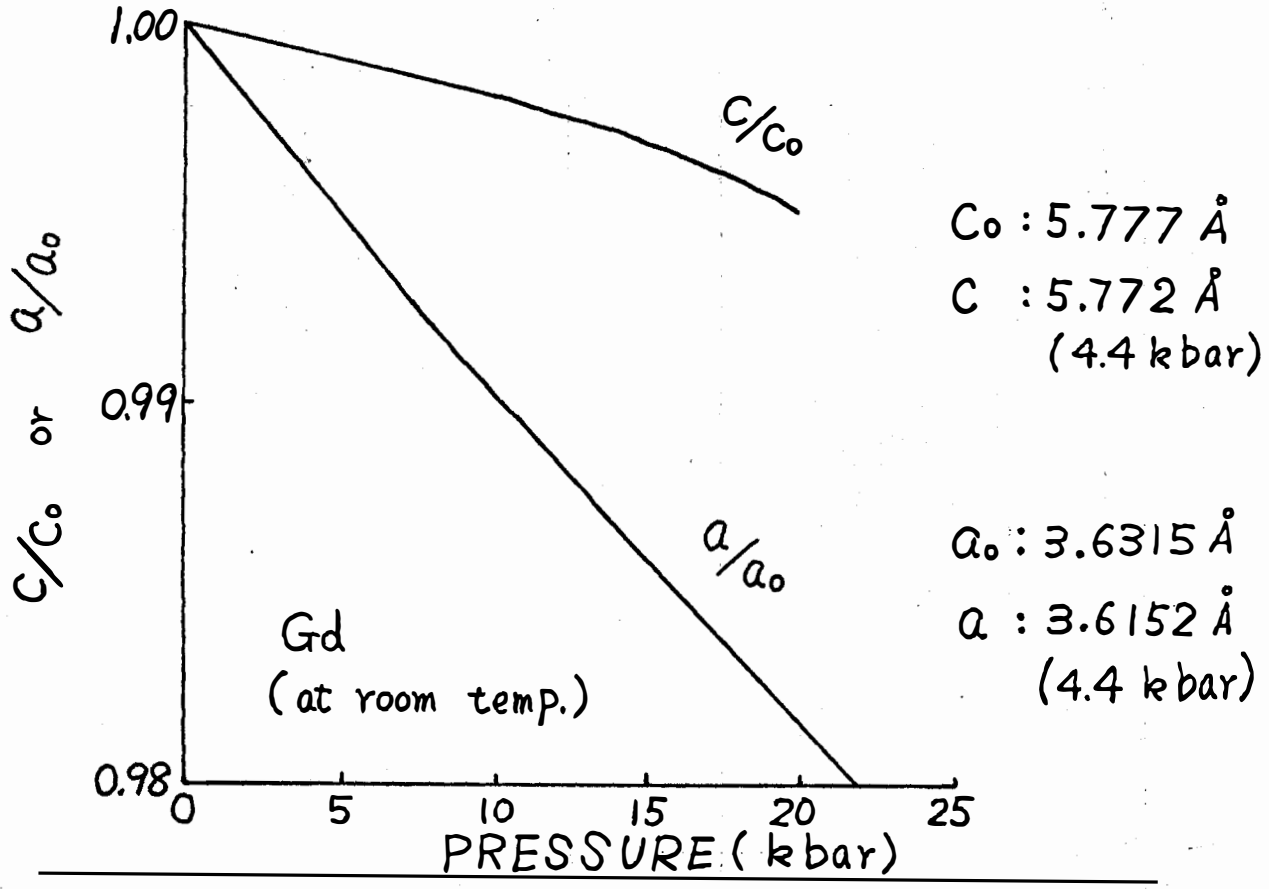


Fig.(4.4) Pressure dependence of c/c_0 and a/a_0 for gadolinium (refer to 69)

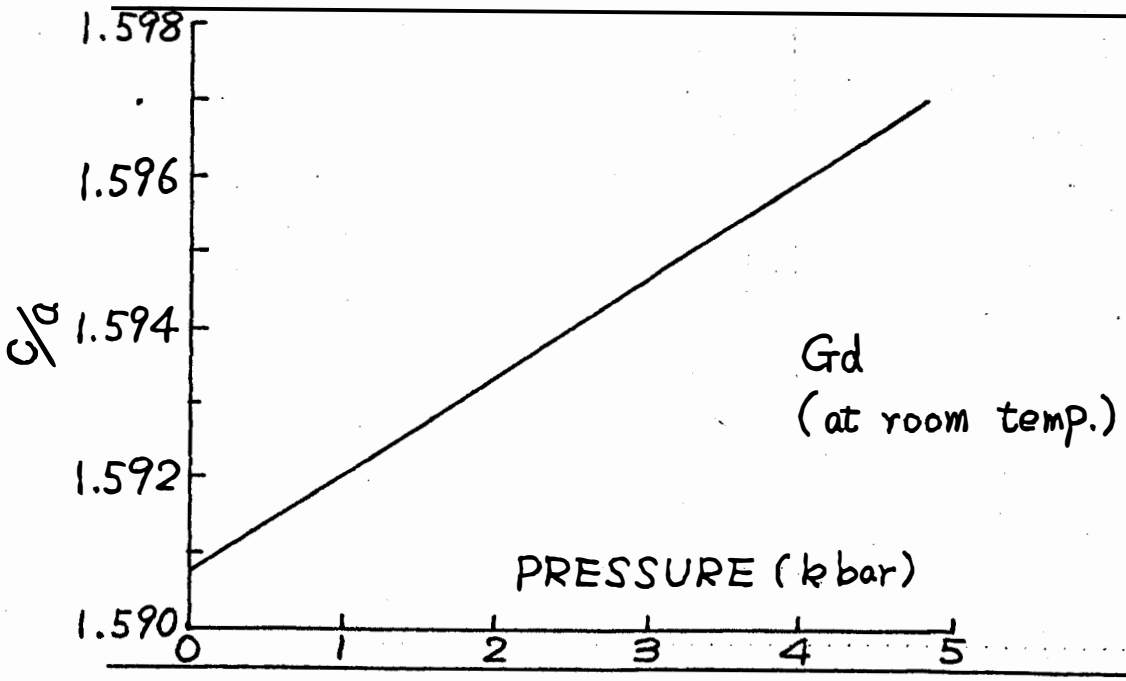


Fig.(4.5); Pressure dependence of c/a for gadolinium

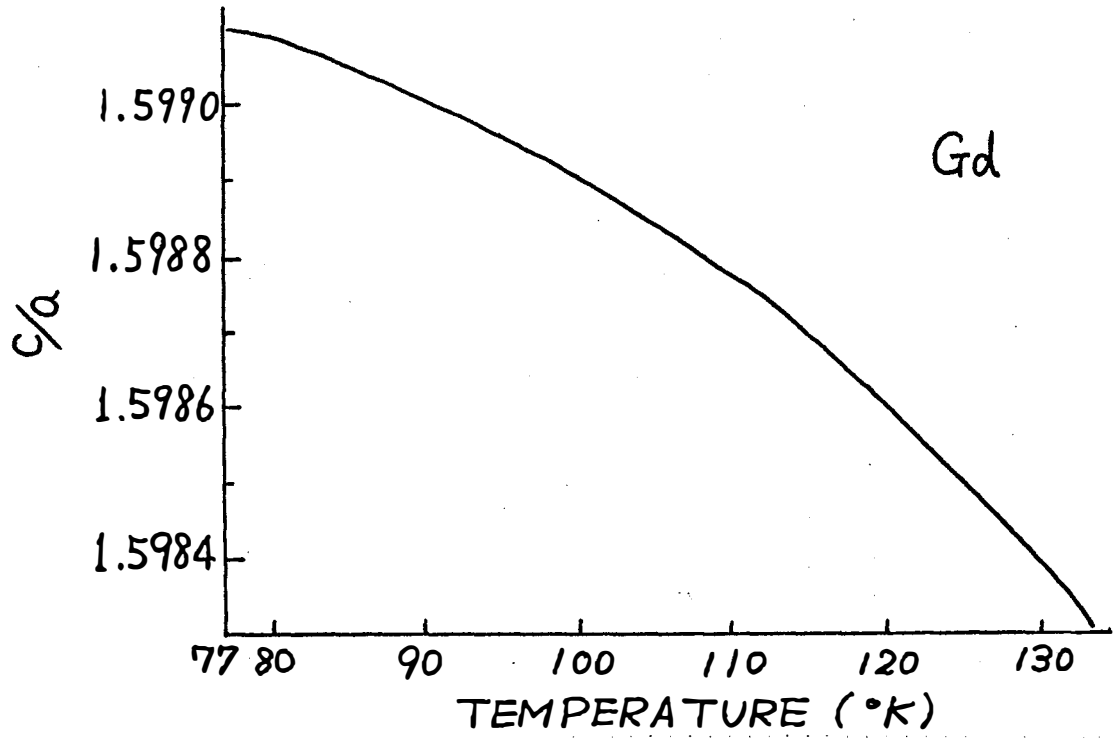


Fig.(4.6); Temperature dependence of c/a for gadolinium (77∿130°K)

The composition dependence of lattice constants of gadolinium-yttrium alloys was measured by Thoburn et al.[58] at room temperature. They reported that the lattice constants of Gd-Y alloys do not change from 10 to 75 at.% yttrium, that is a = 3.64 Å, c = 5.76 Å, c/a = 1.58.

4.2. On the Magnetocrystalline Anisotropy of Gadolinium

In the chapter 3, the experimental results on the anisotropy of Gd have been described.

In this section, a general review on the theories and experiments, which were carried out by other investigators formerly, will be presented and some discussions will be given about the origin of the anisotropy of Gd as well as it's anomalous temperature dependence.

Recently, Brooks and Goodings[47] studied theoretically about the temperature dependence of the anisotropy of Gd on the basis of localized spin model which deals with spin-orbit coupling and dipole-dipole interaction by using higher order perturbation. The results agree with the experimental results for higher term K_2, K_3, in (3-1) expression is good, but the theoretical results fail to interpret the experimental results of the temperature dependence of main term K_1. They suggested that the anomalous behavior of K_1 (T) may arise from an anisotropic field which comes from the anisotropic conduction bands as well as the localized ions.

The author converted the dipole-dipole contribution to the anisotropy into $K_2°$ using the theoretical values (K_1, K_2 or K_3) obtained by Brooks and Goodings[47]. They calculated the anisotropy constant : K_1 due to the dipole-

dipole interaction as follow,

$$K_1(T) = E\left\{\frac{M(T)}{M(O)}\right\}^2$$

where M : magnetization

E : dipole energy for hexagonal close-packed crystal

$$E = -U^2 g^2 \mu_B{}^2 S^2 N / a^3$$

U : dipole factor (in Gd, U = -0.3)

N : total number of atoms per cm^3

a : lattice constant

For Gd (c/a = 1.59),

$$E = 0.729\times10^6 \text{ erg cm}^{-3}.$$

The relation between $K_1(T)$ and $K_2{}^\circ$ (T) is expressed by the following equation

$$K_2{}^\circ = -\frac{2}{3} K_1 .$$

The result is shown in Fig. (4·7). As shown in the figure, it seems that the dipolar anisotropy contributes largely to the origin of the anisotpory of Gd.

Then, the experimental results are discussed. The saturation magnetization of Gd atom has $7.00\mu_B$ due to 4f localized electrons and $0.55\mu_B$ which is considered to be the contribution from conduction electrons, as mentioned in 3.3 section. In the measurement of saturation magnetization of Gd-Y alloys, the saturation magnetization per

Gd atom increases with Y. And the magnetization due to Y atom is $0.20\mu_B$.

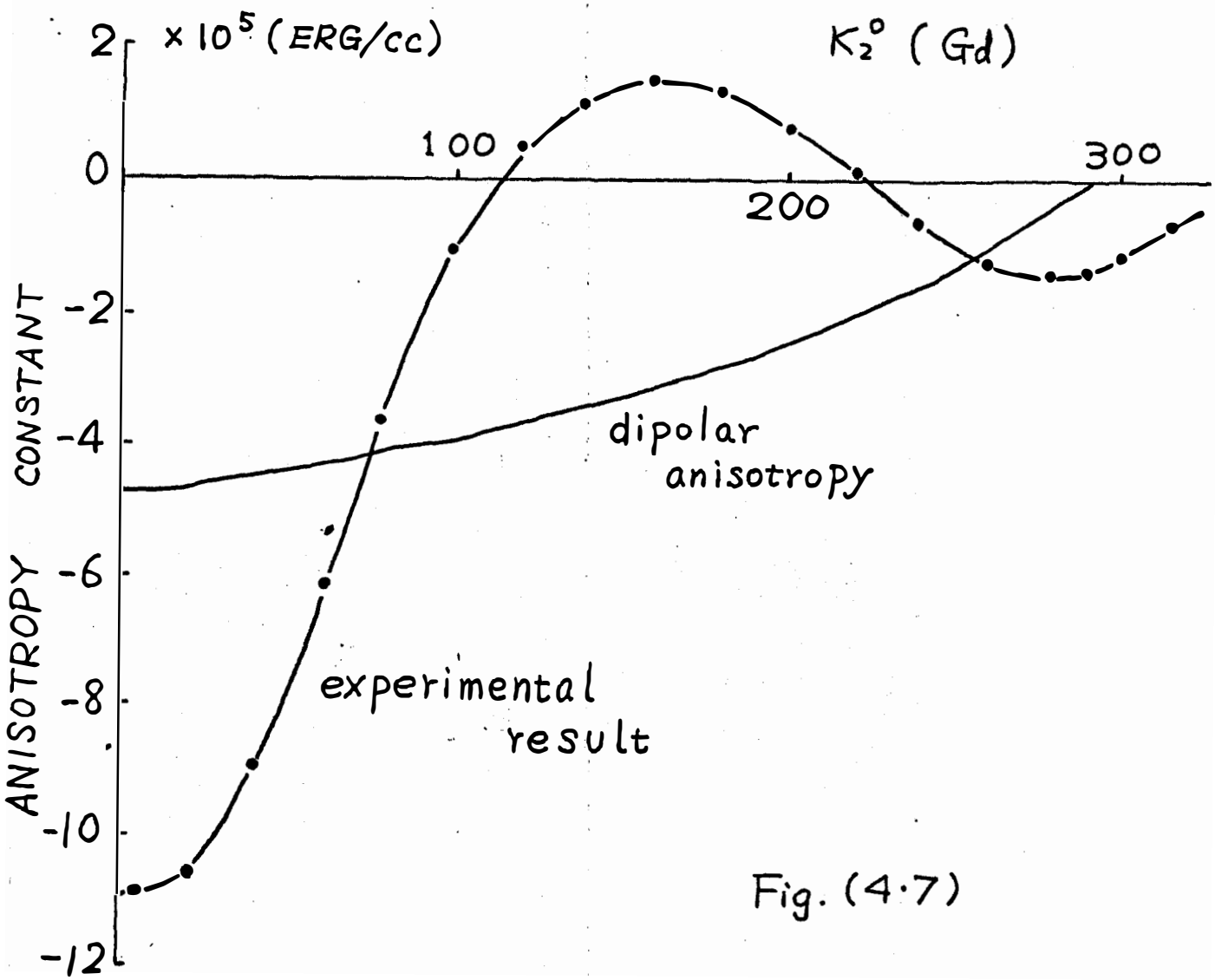


Fig. (4·7)

The value $0.20\mu_B$ is regarded as polarization of the conduction electrons.

The anisotropy of Gd increases with pressure at the Curie point. The author mentions about the effect of

pressure at the ferromagnetic Curie point in Gd of many experiments[68,71~78] and theoretical consideration[82], of late. From their experimental results, the Curie point decreases linearly with pressure in which the order is -1 (°K/kbar) within the critical pressure. Bartholin and Bloch[83] investigated about the effect of uniaxial pressure up to 130 bar using a Gd single crystal and got the following values,

along c-axis : $(\frac{\partial\theta}{\partial p})_c = -(1.55\pm0.05)$ deg/kbar

along a or b-axis : $(\frac{\partial\theta}{\partial p})_a = (\frac{\partial\theta}{\partial p})_b = (0\pm0.05)$ deg/kbar

on the other hand, under hydrostatic pressure,

$(\frac{\partial\theta}{\partial p})_h = -(1.40\pm0.02)$ deg/kbar

From these results, it may be understand that $(\frac{\partial\theta}{\partial p})$ under hydrostatic pressure is mainly due to $(\frac{\partial\theta}{\partial p})_c$, and $(\frac{\partial\theta}{\partial p})_a$ or $(\frac{\partial\theta}{\partial p})_b$ hardly contribute to $(\frac{\partial\theta}{\partial p})_c$.

Recently, Fleming and Liu[82] discussed these phenomena theoretically. They calculated the pressure dependence of the generalized susceptibility function for Gd and explained the change of the Curie point. Fig. (4·8) shows the caluculated result. As shown in the figure (4·8), generalized susceptibility decreases with pressure. This is thought to be due to the change of the energy band of conduction electron.

Returning to the subject of the anisotropy again, by

analogy of the effect of uniaxial and hydrostatic pressure of the Curie point in Gd, the effect of hydrostatic pressure on the magnetocrystalline anisotropy of Gd will be largely due to the contribution of the part concerning c-axis.

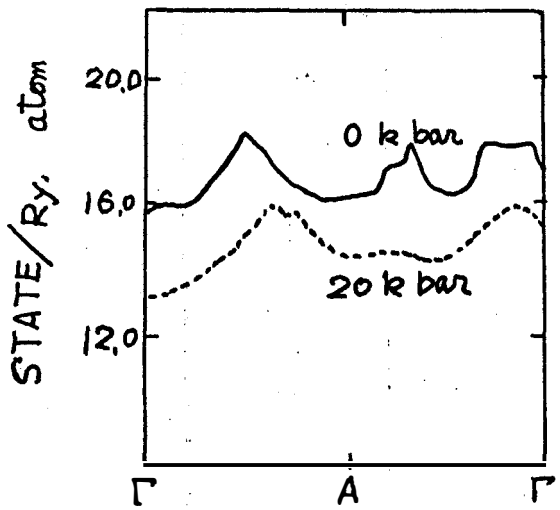


Fig. (4.8) : Generalized susceptibility function for Gd in ΓAΓ direction at 0 and 20 kbar of hydrostatic pressure. (refer to 82)

The large anisotropy of Gd metal in paramagnetic region will be also caused by the conduction electrons on the analogy of the pressure effect of the generalized susceptibility.

The anisotropy constant, $K_2°$, per unit volume of Gd-Y alloys changes linearly at absolute zero and in the case of

70 at.% Gd-30 at.% Y alloy, $K_2°$ becomes larger than that of pure Gd in the absolute value. This phenomenon cannot be explained through the decrease of the saturation magnetization with increasing yttrium contents. However, the saturation magnetization per Gd atom increases linearly with increasing yttrium contents, and the increase is considered to be due to the conduction electrons of Y. Therefore, the drastic change of anisotropy constant at absolute zero temperature is regarded as the contribution from conduction electrons. (Fig. 4·10)

Pearson[83] showed that the temperature dependence of the anisotropy of Gd^{+3} ion in Gadolinium Iron Garnet ($Gd_3Fe_5O_{12}$) can be explained by one-ion model. The crystal structure of $Gd_3Fe_5O_{12}$ is cubic. Gd^{+3} ion in $Gd_3Fe_5O_{12}$ has no conduction electron, so that, the anisotropy of Gd^{+3} ion is considered only localized 4f electrons, while gadolinium metal has conduction electrons.

So far, the author has considered many experimental results to research the origin of the anisotropy of Gd. The anisotropy of Gd seems to be composed of the part which involves the contribution explainable by one-ion model and the contribution of dipole-dipole interaction, and the part due to conduction electrons. The complicated temperature dependence as shown in figure (3·1) may be originated from the temperature dependence of the above two terms, respect-

ively. Then, it is investigated about the connection of the Fermi surface of gadolinium. Freeman et al.[84] calculated the Fermi surface of thulium by using the APW method as figure (4·9). Afterwards, Keeson et al.[85] pointed out that the Fermi surface as shown in figure (4·9) is similar to that of Gd.

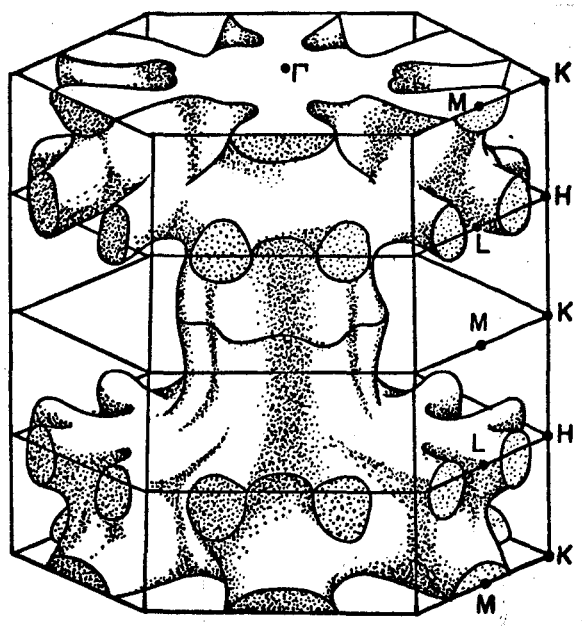


Fig. (4·9) : The complete Fermi surface for hole in Tm metal in the double zone representation (refer to 84)

The author will consider, next, the effect of hydrostatic pressure on Gd. As discussed previously, hydrostatic pressure will (decrease the Curie point) mainly along the c-axis as the pressure effect of the Curie point. As shown in figure (4·9), the trunk provides the Fermi surface parallel to the c-axis while the arms are responsible for that perpendicular to it. Pressure reforms a part of arms drastically, and has influence on anisotropic field depending upon anisotropic conduction bands.

The anisotropy under high pressre changes with temperature drastically. The shape of Fermi surface in figure (4·9) will be changed through the s-f exchange interaction. If the origin of the anisotropy of Gd is consisted of the contribution from 4f electrons and that of conduction electrons, both will change by the application of pressure.

The magnetic dipole-dipole contribution to the anisotropy was estimated as shown in figure(4·7). How much is the contribution of the conduction electrons to the anisotropy? The author will estimate it from the anisotropy of Gd-Y alloys as a criterion. As shown in figure (3·5), the anisotropy constant changes drastically with the increase of Y. The apparent anisotropy of Y is estimated using figure (3·5). Figure (4·11) shows the experimental values of 10, 20 and 30 at.% Y minus the value which is multiplied 0.9, 0.8 and 0.7 to the anisotropy constant of pure gagolinium. The apparent anisotropy of Yttrium is regarded to change linearly. The contribution to the anisotropy from one yttrium atom is regarded approximately as constant independent of the concentration. The anisotropy constant per Y atom has been got from 30 at.% Y data in Fig. (4·11). The result is shown as the curve (A) in Fig.(4·12). Yttrium itself has no magnetocrystalline anisotropy since it is non-magnetic itself. If the contribution of yttrium conduction electrons

to the anisotropy is assumed to be the same that of Gd, the apparent anisotropy (A) of Y in Fig. (4·12) would be estimated as the contribution to the anisotropy of conduction electrons. The anisotropy per Gd atom is shown in Fig. (4·12). If the origin of anisotropy of Gd arises from both conduction electrons and 4f electrons, the anisotropy of 4f electrons would be the difference between the experimental value and the contribution from conduction electrons. The anisotropy of 4f electrons is shown as the curve (B) in Fig. (4·12).

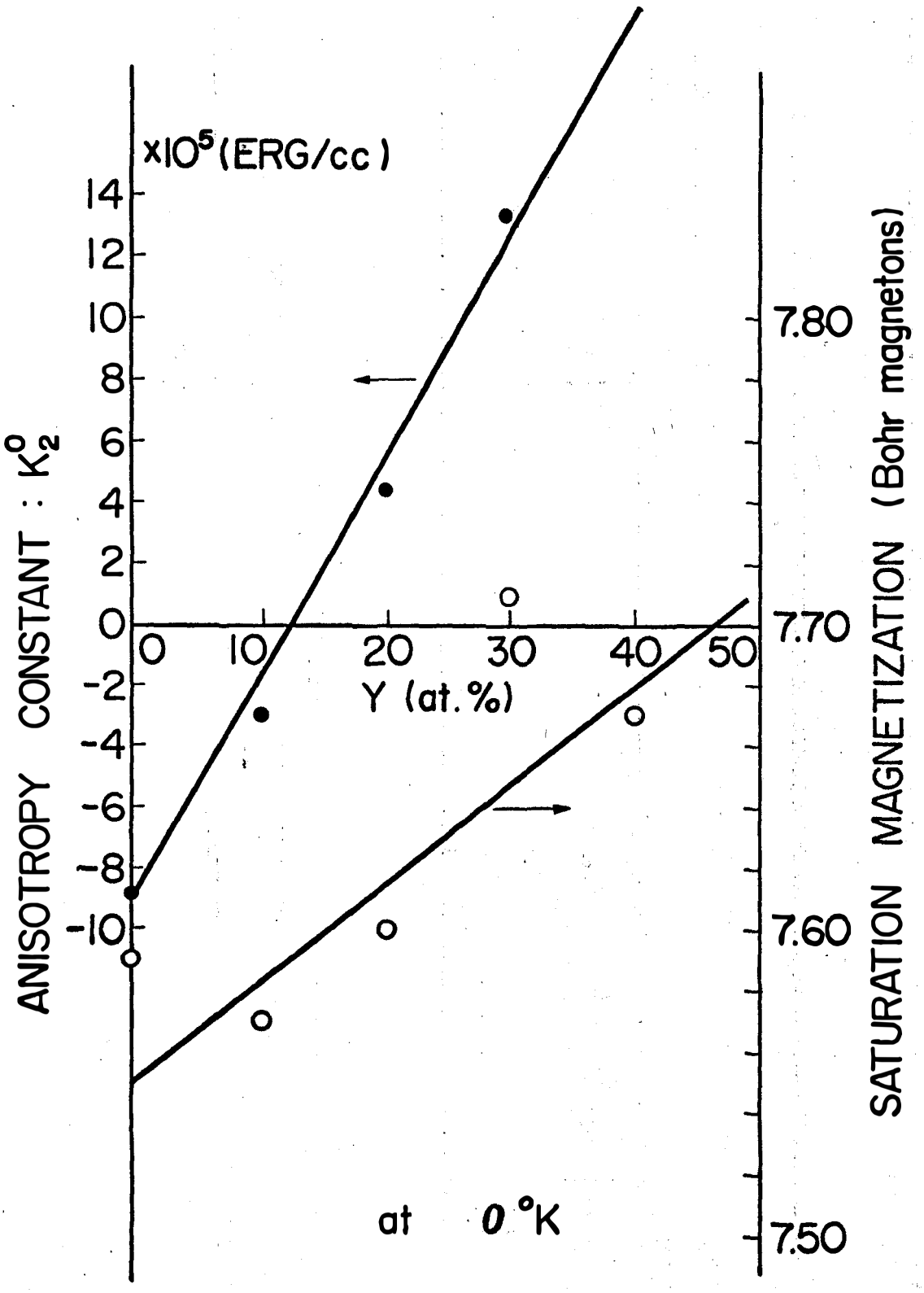


Fig.(4·10) Gd–Y alloys

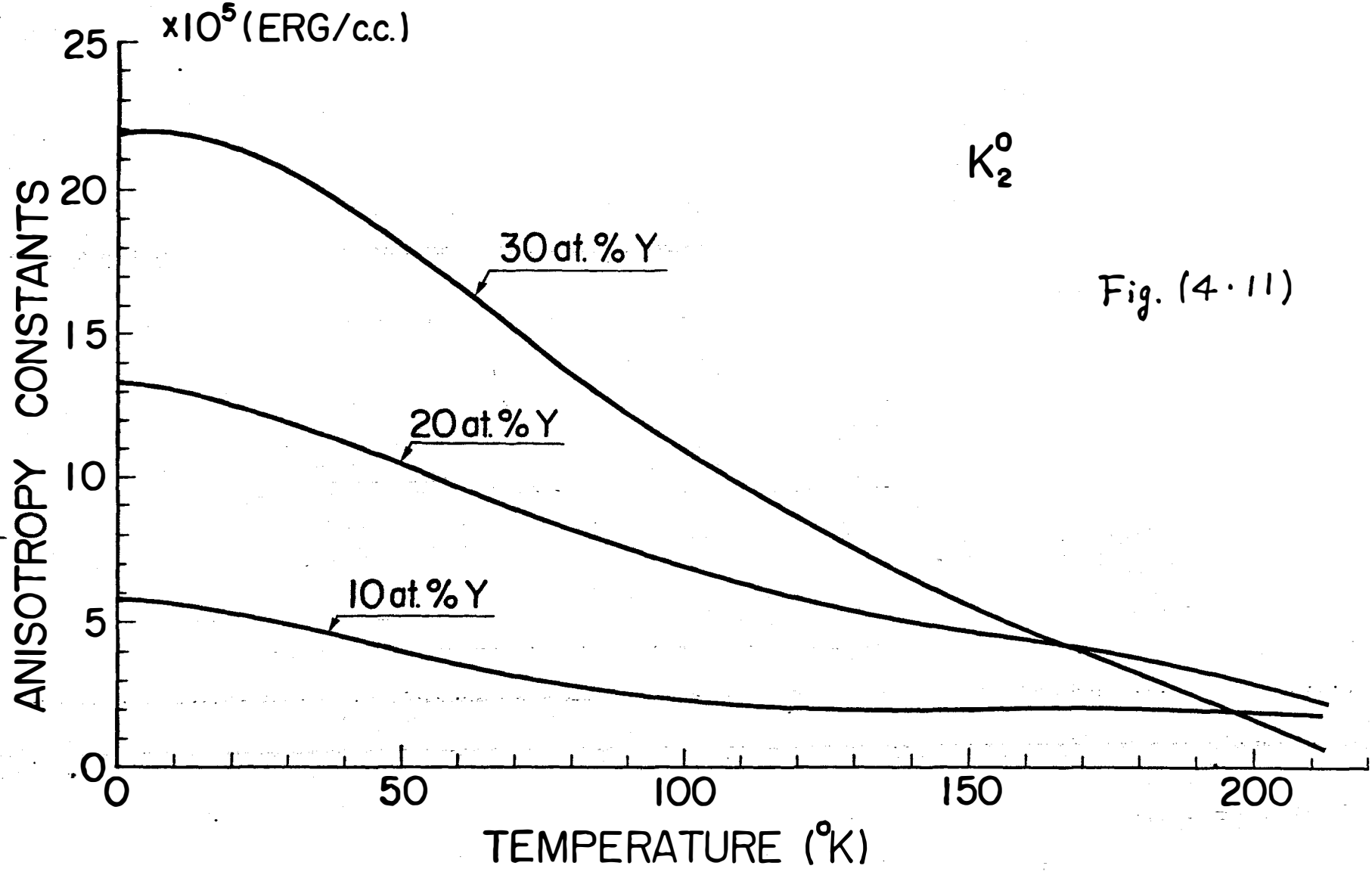


Fig. (4·11)

Contribution of Y to the anisotropy constants of Gd

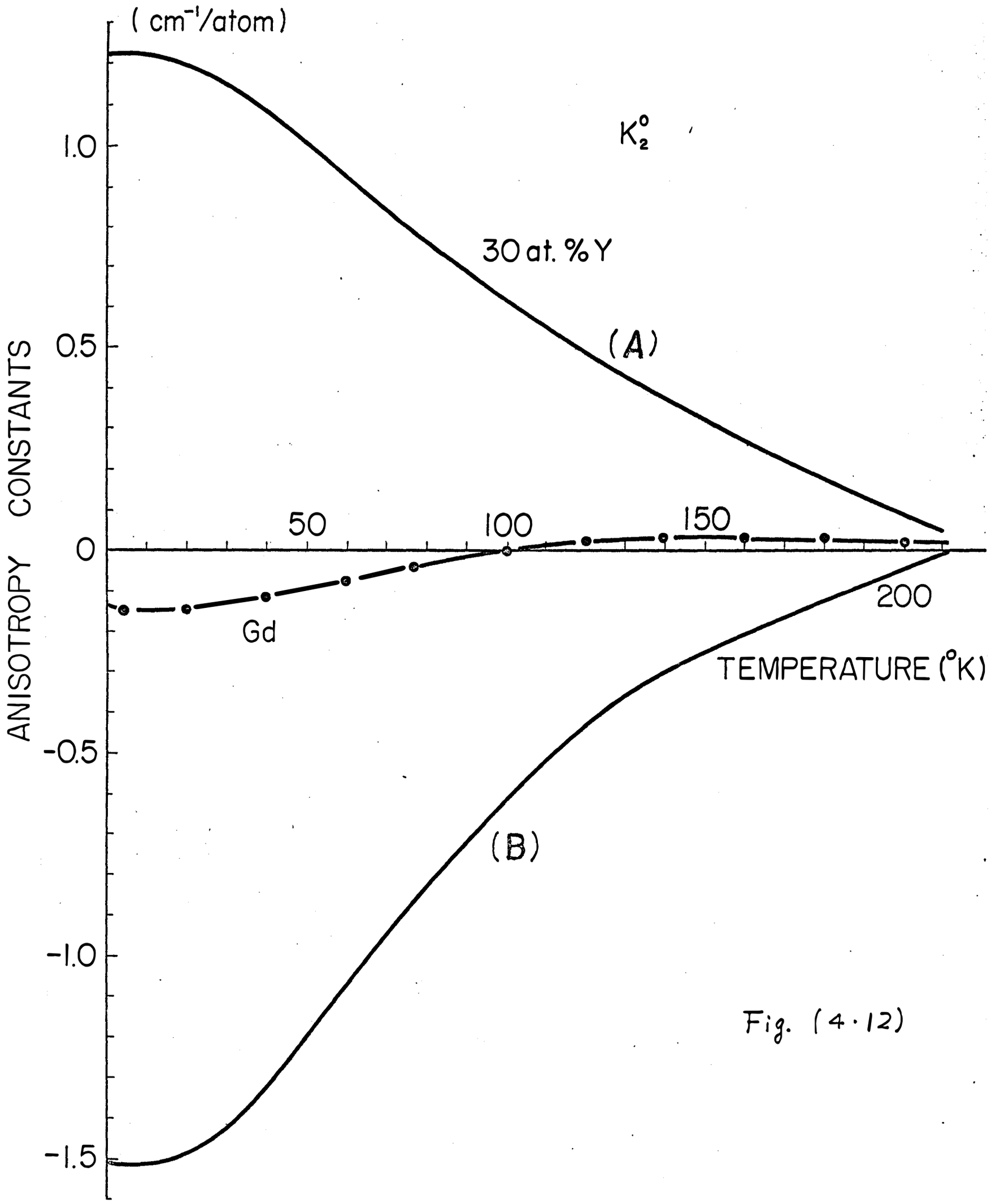

(cm⁻¹/atom)
1.0
0.5
0
-0.5
-1.0
-1.5
ANISOTROPY CONSTANTS
K_2^0
30 at. % Y
(A)
(B)
Gd
50
100
150
200
TEMPERATURE (°K)

Fig. (4·12)

Chapter 5 : CONCLUSION

In order to investigate the origin of the magnetocrystalline anisotropy of Gd, the following two experiments were made in the present work.

(i) Temperature dependence of the magnetocrystalline anisotropy of Gd-Y alloys.

The basic idea of this measurement was that alloying of non-magnetic Y metal into the Gd would reduce the magnetization and anisotropy if the anisotropy of Gd could be explained by the one-ion model. The reason why Y was chosen as the diluting material is that it has almost the same structure, lattice parameter, atomic volume as Gd, so that the addition of Y increases average Gd-Gd distance and gives a certain effect on the magnetic interaction between Gd atoms.

(ii) Pressure dependence of the magnetocrystalline anisotropy of pure Gd.

The experimental value $7.55\mu_B$ of the saturation moment for Gd is significantly higher than the theoretical value $7.00\mu_B$ obtained from the spin angular momentum. The difference $0.55\mu_B$ is considered to be due to the polalization of the conduction electrons. From measurements of the magnetization of Gd-Y alloys, it was estimated that Y had the magnetic moment of $0.20\mu_B$ per atom, which was considered to be the contribution of the conduction electrons of Y.

It was found that the addition of non-magnetic constituent Y causes a drastic change in the temperature dependence of the anisotropy of Gd-Y alloys. The anisotropy constant of 30 at. % Y is larger than the value for pure Gd at 0°K. It can not be explained by the change of the magnetic moment.

In the magnetic properties of Gd, the conduction electrons play a very important role and it is thought to take a large part in the anisotropy. The anisotropy due to the conduction electrons could be estimated in Gd-Y alloys, provided that the contribution to the anisotropy of the conduction electrons of Y is the same as that of Gd. On the other hand, the anisotropy due to the dipole-dipole interaction in pure Gd was estimated by Brooks et al.. The calculated value by them shows about -5×10^5 erg/cc and the experimental value in the present work exhibits about -11×10^5 erg/cc.

In conclusion, the magnetocrystalline anisotropy of Gd is considered to be caused by two terms, i.e., localized 4f electrons and conduction electrons. The temperature dependence of the anisotropy of pure Gd under hydrostatic pressure exhibited a very complicated behavior, which is considered to result from the change of the contribution of these two origins by pressure.

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