

## Temperature Dependence of Ferromagnetic Anisotropy

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The temperature dependence of the crystalline anisotropy constants of iron, cobalt, and nickel is discussed. It is shown that Zener's result for iron (i.e., the first anisotropy constant varies as the tenth power of the magnetization) also may be derived from molecular field theory. In cobalt a satisfactory agreement with experiment is obtained by using Zener's results together with the postulate that the intrinsic anisotropy varies with thermal expansion in the manner recently calculated by the author. For nickel the temperature dependence of  $K_1$  seems to require, in addition to the tenth power of the magnetization, a multiplicative factor that is linear in the temperature. No explanation has been found for this latter term.

### INTRODUCTION

THE crystalline anisotropy energy of most ferromagnets is a rapidly varying function of temperature; much more so, for example, than the spontaneous magnetization. This fact has stimulated a considerable interest in the problem and has led to a number of previous theories which are discussed below.

The anisotropy energy is described by "anisotropy constants" in an expansion of the free energy in elements of crystal symmetry. For a cubic crystal at a temperature  $T$ , the free energy, in terms of the direction cosines of magnetization  $\alpha_i$ , is given by

$$F = F_0(T) + K_1(T)(\alpha_1^2\alpha_2^2 + \alpha_1^2\alpha_3^2 + \alpha_2^2\alpha_3^2) + K_2(T)\alpha_1^2\alpha_2^2\alpha_3^2 + \dots \quad (1)$$

The energy

$$F = F_0(0) + K_1(0)(\alpha_1^2\alpha_2^2 + \alpha_1^2\alpha_3^2 + \alpha_2^2\alpha_3^2) + K_2(0)\alpha_1^2\alpha_2^2\alpha_3^2 + \dots \quad (2)$$

at  $T=0$  is of special interest since in this case the atomic moments are aligned parallel and  $K_1(0)$ ,  $K_2(0)$ , etc., are a measure of the intrinsic anisotropic coupling between spins.

The discussion for cubic materials will be confined largely to the first constant  $K_1$  since the subsequent terms are smaller, and only  $K_1$  is known experimentally over a wide temperature range. The temperature range of interest extends to a value somewhat smaller than the Curie temperature, since near  $T_c$  even the constant  $K_1$  becomes very small and inconsequential.

### (A) Theory of Zener

The calculations of Akulov<sup>1</sup> and of Zener<sup>2</sup> have given a clear understanding of the physical principle involved in the rapid decrease of anisotropy with temperature in iron.

Akulov observed that as  $T \rightarrow 0$  Eq. (1) can be derived from Eq. (2) if the spins are thought of as completely aligned but precessing about the applied field. For such a case he showed that  $K_1(T)/K_1(0)$  would approach

zero temperature as the tenth power of the reduced magnetization,  $I/I_0$ , in agreement with experiment.

Zener carried this idea much further by supposing that over the whole temperature range there exists a short-range ordering of spins about each atom and thus, if the  $\alpha_i$  in (2) are taken to be direction cosines of the ordered spins, it is necessary only to average properly over all the directions of short-range order to obtain (1), where the  $\alpha_i$  in (1) refer to the bulk magnetization. Thus Zener obtained the result

$$K_1(T)/K_1(0) = (I/I_0)^{10}, \quad (3)$$

for the complete  $K_1$  vs  $T$  curve, in excellent agreement with experiment for iron.

Some details in this theory will be considered more closely in the following section, where approximately the same result is derived by a different type of averaging.

### (B) Work of Van Vleck

Much of the pioneering work on anisotropy has been done by Van Vleck.<sup>3</sup> In essence Van Vleck starts with an approach in which two spins are coupled by pseudo-dipolar and pseudo-quadrupolar interactions. The free energy is then calculated by developing the partition function in powers of  $T^{-1}$  and by treating the above interactions as perturbations.

The key point in the calculation occurs with replacement of the exchange interaction by a molecular field, which allows the unperturbed state to be one in which the individual spins are quantized separately. Another approximation is made in which a small amount of correlation among neighboring spins is introduced. Keffer<sup>4</sup> has pointed out that the lack of sufficient spin correlation makes the dipolar part of Van Vleck's calculation depend too strongly upon temperature, and the quadrupolar part not strongly enough.

### (C) Other Methods

A logical extension to Van Vleck's work is the evaluation of the pseudo-polar couplings by means of

<sup>1</sup> N. S. Akulov, Z. Physik **100**, 197 (1936).

<sup>2</sup> C. Zener, Phys. Rev. **96**, 1335 (1954).

<sup>3</sup> J. H. Van Vleck, Phys. Rev. **52**, 1178 (1937).

<sup>4</sup> F. Keffer, Phys. Rev. **100**, 1692 (1955).

spin waves. Such calculations have been made by Pal<sup>5</sup> and Keffer,<sup>4</sup> both of whom obtained the tenth power law for the cubic case, and by Kasuya<sup>6</sup> who obtained a sixteenth power law. These results apply only in the limited range of low temperatures.

Pal treats the temperature dependence of cobalt as a competition between dipole-like and quadrupole-like terms; whereas Vonsovsky<sup>7</sup> considers the excitation of electrons to higher orbital states.

Other calculations to be considered later are those of Sato and Tino,<sup>8</sup> and Brenner.<sup>9</sup>

#### Anisotropy of Iron

The method used by Zener to derive the temperature dependence of anisotropy is a general one, independent of the type of coupling between atoms, except that the atomic coupling constants are assumed to be independent of temperature. A questionable point in the argument is the use of a random-walk distribution function to describe the motion of magnetization within a small volume element of the crystal. It is desired to show that essentially the same result may be obtained from molecular field theory.

For a large crystal the anisotropy energy of each eigenstate may be written as the interaction of an atom with its surroundings, multiplied by the number of atoms. Let the volume of the "surroundings" be designated by  $G$ . Clearly,  $G$  must be as large in linear dimensions as the range of the anisotropy forces and evidently corresponds to the unspecified volume element considered by Zener. The key assumption which reduces the problem to a very simple classical one is that, for the eigenstates of interest below the Curie temperature, the spins in the region  $G$  are highly correlated. Thus, the local magnetization,  $I_l$ , approximately satisfies  $I_l^2 = I_0^2$ , where  $I_0$  is the magnetization of the crystal at  $T=0$ .

For definiteness one may think of the region  $G$  as containing an atom, and several shells of nearest neighbors. The most convincing evidence for presuming the spins are ordered in a region of this size is the observation, from neutron scattering, that magnetically coherent regions of several unit cells in size exist even at the Curie point.<sup>10</sup> Additional evidence has been discussed by Keffer.<sup>4</sup>

Thus, the anisotropy of the atom at the center of  $G$  is obtained from Eq. (2) if the  $\alpha_i$  are replaced by  $\beta_i$ , which refer to the local magnetization.

Since the component of magnetization in the field direction in  $G$  must be the same as the bulk magnetization  $I$ , evidently the local magnetization of magni-

tude  $I_0$  can be thought of as precessing about the direction of the field with an average polar angle  $\Theta$  given by

$$\langle \cos \Theta \rangle = I/I_0. \quad (4)$$

It is necessary to average (2) over this precessional motion and over the spread of angles  $\Theta$  to obtain the bulk anisotropy. At this point, it is not entirely apparent that the result will be correctly a component of the free energy, but such is shown to be the case in the Appendix. The average over the azimuthal angle is readily performed,<sup>2</sup> leading to

$$K_1(0) \langle \beta_1^2 \beta_2^2 + \beta_1^2 \beta_3^2 + \beta_2^2 \beta_3^2 \rangle = \frac{1}{3} K_1(0) [1 - \langle P_4(\cos \Theta) \rangle] + K_1(0) \langle P_4(\cos \Theta) \rangle (\alpha_1^2 \alpha_2^2 + \alpha_1^2 \alpha_3^2 + \alpha_2^2 \alpha_3^2), \quad (5)$$

and therefore

$$K_1(T) = K_1(0) \langle P_4(\cos \Theta) \rangle, \quad (6)$$

where  $P_4$  is the fourth-order Legendre polynomial. Zener calculated  $\langle P_4 \rangle$  by assuming the local magnetization undergoes a random walk, subject to the side condition that  $\langle \cos \Theta \rangle$  is equal to the measured  $I/I_0$ . Alternatively, the averaging may be performed, in the manner of Brenner,<sup>9</sup> by using a more conventional distribution function obtained from molecular field theory.\* Since the local magnetization is a large quantum number, the classical or Langevin function is the appropriate one to use. Thus

$$\begin{aligned} \langle P_4(\cos \Theta) \rangle &= \frac{\int_0^\pi P_4(\cos \Theta) e^{\alpha \cos \Theta} \sin \Theta d\Theta}{\int_0^\pi e^{\alpha \cos \Theta} \sin \Theta d\Theta} \\ &= \frac{P_4(\partial/\partial \alpha) Z}{Z}, \end{aligned} \quad (7)$$

where  $Z = (2/\alpha) \sinh \alpha$  is the partition function, and  $\alpha(T)$  is  $(kT)^{-1}$  times the "averaged" interaction between the local magnetization and the remainder of the crystal at a particular temperature; or in other words, the product of  $(kT)^{-1}$  and the magnetic moment times the molecular field.

After the differentiation indicated in (7), the result may be written as

$$\langle P_4(\cos \Theta) \rangle = 1 + \frac{35}{\alpha^2} - \left( \frac{10}{\alpha} + \frac{105}{\alpha^3} \right) \frac{I}{I_0}, \quad (8)$$

with  $I/I_0$  substituted for  $\coth \alpha - 1/\alpha$ , which is the explicit expression for  $\langle \cos \Theta \rangle$ .

For the present calculation let  $\alpha$  be that function of temperature which exactly reproduces the observed

\* Keffer (reference 4) also has given results for this type of averaging in the general case of an  $n$ th-order polynomial.

<sup>5</sup> L. Pal, Acta Phys. Acad. Sci. Hung 3, 294 (1954).

<sup>6</sup> T. Kasuya, J. Phys. Soc. (Japan) 2, 944 (1956).

<sup>7</sup> S. V. Vonsovsky, J. Phys. (U.S.S.R.) 3, 83 (1940).

<sup>8</sup> M. Sato and Y. Tino, J. phys. radium 17, 5 (1956).

<sup>9</sup> R. Brenner, Phys. Rev. 107, 1539 (1957).

<sup>10</sup> C. G. Shull, in *Les Electrons Dans Les Metaux*, edited by R. Stoops (Coudenberg, Bruxelles, 1955), p. 227.

magnetization, i.e., which satisfies

$$\coth\alpha - 1/\alpha = (I/I_0)_{\text{meas.}} \quad (9)$$

The results substituted into (8) are plotted in Fig. 1, giving good agreement with the measured  $K_1(T)$  over the entire temperature range. In effect, the calculated curve of Fig. 1 results from substituting the measured magnetization into the calculated expression for  $\langle P_4 \rangle$ , written as a function of the calculated magnetization. The reason these points are quite different from those calculated by Brenner<sup>9</sup> is that Brenner used the Weiss field approximation for  $\alpha$ , rather than the experimentally determined values used here. It is interesting to note that this difference in the partition function, which introduces only a small error in  $\langle \cos\Theta \rangle$ , leads to a large discrepancy in the average of the anisotropy energy. In fact, at low temperatures, the difference between the curve in Fig. 1 and Brenner's curve is just ten times the difference between the usual Langevin function and the measured magnetization. The result points out the difficulty of a calculation on the temperature dependence of anisotropy based entirely on quantum mechanical first principles, without relating the results to other measured quantities.

It is of further interest to understand why the molecular field averaging agrees with Zener's tenth power law. This fact is understood when it is observed that over the temperature range of principal interest ( $T/T_c \leq 0.8$ ),  $\coth\alpha$  may be replaced by unity and

$$I/I_0 \simeq 1 - 1/\alpha. \quad (10)$$

Thus

$$\left(\frac{I}{I_0}\right)^{10} \simeq 1 - \frac{10}{\alpha} + \frac{45}{\alpha^2} - \frac{120}{\alpha^3} + \frac{210}{\alpha^4} - \dots, \quad (11)$$

while with the same approximation, from (8),

$$\langle P_4(\cos\Theta) \rangle \simeq 1 - \frac{10}{\alpha} + \frac{45}{\alpha^2} - \frac{105}{\alpha^3} + \frac{105}{\alpha^4} - \dots, \quad (12)$$

the first three terms in (12) agreeing exactly with those of (11), and the succeeding terms having order of magnitude agreement.

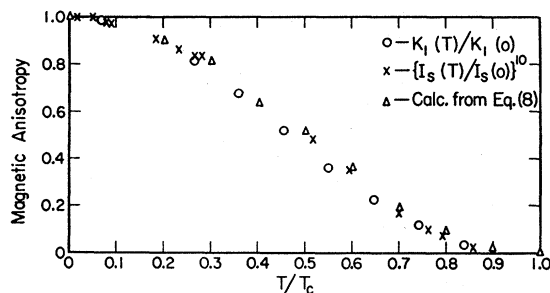


FIG. 1. Comparison of experimental curve, the tenth power law (taken from Zener<sup>2</sup>) and the result of molecular field averaging for the temperature dependence of  $K_1$  in iron.

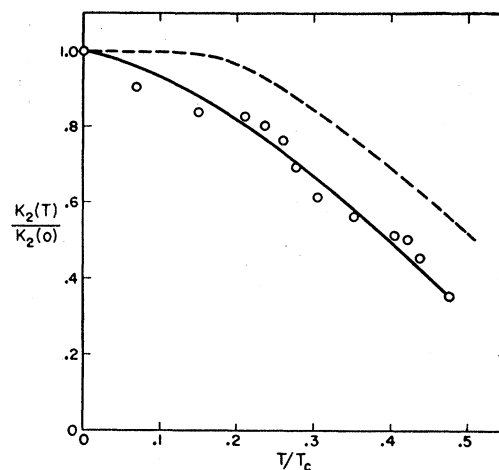


FIG. 2. Comparison of the second anisotropy constant of cobalt with a tenth power law. --- Tenth power of the reduced magnetization, from measurements by H. P. Meyers and W. Sucksmith (reference 13). — Anisotropy as a function of temperature according to recent (1954) data of Sucksmith and Thompson. This curve differs considerably from the older measurements of Honda and Masumoto (1931) and Gans and Czerlinski (reference 12).

Thus, it is shown that in Zener's calculation the random walk approximation is not a critical part of the theory.<sup>11</sup> Near the Curie point the molecular field result seems to differ somewhat from the tenth power law, but the measurements of magnetization are not precise enough to determine which is in better agreement with the experimental curve.

#### Hexagonal Cobalt

The free energy of hexagonal cobalt has the symmetry

$$F = F_0 + K_1 \sin^2\Theta + K_2 \sin^4\Theta + \dots, \quad (13)$$

with  $\Theta$  the angle between magnetization and the  $c$  axis. When averaged over the motion of the local magnetization the following expressions result for the temperature dependence of the anisotropy constants,

$$K_1(T) = \left( K_1(0) + \frac{8}{7} K_2(0) \right) \left( \frac{I}{I_0} \right)^3 - \frac{8}{7} K_2(0) \left( \frac{I}{I_0} \right)^{10} + \dots \simeq K_1(0) (I/I_0)^3, \quad (14)$$

$$K_2(T) = K_2(0) (I/I_0)^{10} + \dots. \quad (15)$$

The above formulas were obtained by using the random walk distribution, but no essential difference arises from a molecular field function.

<sup>11</sup> At low temperatures it is unnecessary to consider a distribution function at all, since for small  $\Theta$ ,  $\langle \cos^n\Theta \rangle \simeq (\cos\Theta)^n$  and thus  $K_1(T)/K_1(0) = \langle P_4(\cos\Theta) \rangle \simeq P_4(I/I_0)$ , which is the result of Akulov. The experimental anisotropy for iron, in fact, does agree with  $P_4(I/I_0)$  up to  $T/T_c \sim 0.5$ . If  $I$  is written as  $I_0 - \Delta I$ , it readily may be shown that as  $T \rightarrow 0$ ,  $P_4(I/I_0) \rightarrow 1 - 10(\Delta I/I_0)$ , giving the tenth power law.

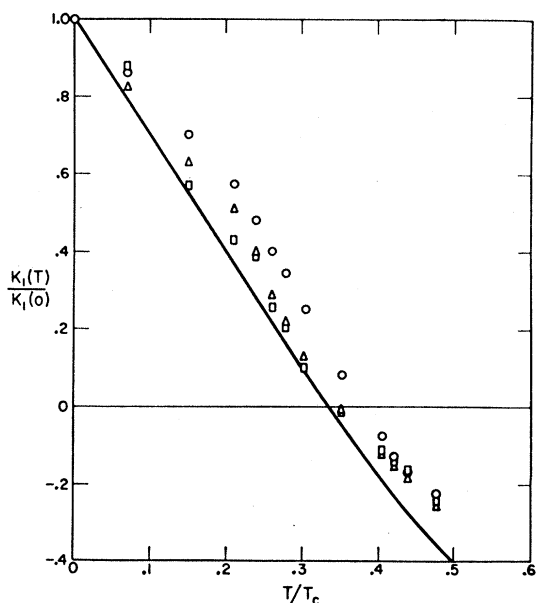


FIG. 3. Temperature dependence of  $K_1$  for cobalt. — Calculated from Eq. (23);  $\circ$  experimental data of Sucksmith and Thompson (reference 12);  $\triangle$  data from Honda and Masumoto as given in reference 12;  $\square$  data from Gans and Czerlinski as given in reference 12.

Experimentally it is difficult to separate  $K_2$  from the larger  $K_1$  term in the anisotropy, and the data<sup>12</sup> of various investigators on  $K_2(T)$  do not agree. This, together with the uncertainties in the magnetization as a function of temperature for cobalt,<sup>13</sup> prevents an accurate check of Eq. (15). Nevertheless, the most recent data by Sucksmith and Thompson<sup>12</sup> are in rough agreement with a tenth power law, as shown in Fig. 2.

The formula (14) for  $K_1(T)$  obviously does not describe the experimental points shown in Fig. 3, since the latter decrease much more rapidly and change sign at about 500°K. It is apparent, therefore, that the intrinsic anisotropy, itself, is a function of temperature; i.e., the coupling between atoms with parallel spins changes with  $T$ . To understand such an effect, it is, of course, necessary to consider an atomic theory of anisotropy. In a recent calculation,<sup>14</sup> the author developed a theory somewhat along the lines of a model illustrated by Kittel<sup>15</sup> in which each atom, in consequence of its orbital angular momentum, has a distorted charge distribution that is coupled to the spin. These charge distributions interact among each other and with the crystalline field to produce the anisotropy. In cobalt, the principle interaction was calculated to be that between the distorted charge cloud and the

crystalline field of the lattice, the result being

$$K_1(0) = CS_{22} - (12/7)K_2(0), \quad (16)$$

where  $C$  is a constant and  $S_{22}$  a lattice sum which is a measure of the crystalline field. Some years ago it was pointed out by McKeehan<sup>16</sup> that the particular lattice sum involved here is highly strain sensitive in the case of cobalt. It is tempting, therefore, to attribute the change in sign of  $K_1$  as due to thermal expansion. In analogy with (14) let the anisotropy constant be described by

$$K_1(T) = \left[ CS_{22}(T) - \frac{12}{7}K_2(0) \right] \left( \frac{I}{I_0} \right)^3, \quad (17)$$

where the term in the brackets is the intrinsic anisotropy, depending upon temperature through strain, and the factor  $(I/I_0)^3$  again results from the local magnetization not being fully aligned with the field. To agree with measurements at  $T=0$ , the constant  $C$  must have the value

$$\frac{K_1(0) + (12/7)K_2(0)}{S_{22}(0)},$$

and thus

$$K_1(T) = \left\{ \left[ K_1(0) + \frac{12}{7}K_2(0) \right] \frac{S_{22}(T)}{S_{22}(0)} - \frac{12}{7}K_2(0) \right\} \left( \frac{I}{I_0} \right)^3. \quad (18)$$

Taking  $K_2(0)/K_1(0) = 0.28$ , which is an average value from three sets of measurements,<sup>12</sup> one obtains

$$\frac{K_1(T)}{K_1(0)} = \left\{ 1.48 \frac{S_{22}(T)}{S_{22}(0)} - 0.48 \right\} \left( \frac{I}{I_0} \right)^3. \quad (19)$$

According to McKeehan, the lattice sum depends upon  $M$ , the  $c/a$  ratio, in the manner

$$S_{22} = 0.00507 - 5.42(M - 1.633)/1.633, \quad (20)$$

if  $M$  is close to the value for ideal packing, 1.633. Letting  $M = M_0(1 + \alpha T)$ , where  $\alpha$  is an average thermal expansion coefficient for  $c/a$ , one obtains

$$S_{22} = 0.00507 - 3.32(M_0 - 1.633) - 3.32M_0\alpha T, \quad (21)$$

and finally

$$\frac{K_1(T)}{K_1(0)} \sim \left\{ 1 - \frac{4.9M_0\alpha T}{0.00507 - 3.32(M_0 - 1.633)} \right\} \left( \frac{I}{I_0} \right)^3. \quad (22)$$

In the absence of data for the complete temperature range, a value  $3.5 \times 10^{-6}$  will be used for  $\alpha$ , which has

<sup>12</sup> W. Sucksmith and J. E. Thompson, Proc. Roy. Soc. (London) **A225**, 362 (1954).

<sup>13</sup> H. P. Meyers and W. Sucksmith, Proc. Roy. Soc. (London) **A207**, 427 (1951).

<sup>14</sup> W. J. Carr, Jr., Phys. Rev. **108**, 1158 (1957).

<sup>15</sup> C. Kittel, *Introduction to Solid State Physics* (John Wiley and Sons, Inc., New York, 1956), second edition, p. 429.

<sup>16</sup> L. W. McKeehan, Phys. Rev. **43**, 1025 (1933); **52**, 18 (1937).

been measured in the range 33 to 100°C.<sup>17</sup> For solid cobalt the more recent measurements by Owen and Jones<sup>18</sup> furnish a room temperature value for  $c/a$  of 1.6322. Extrapolating this result back to absolute zero, one obtains  $M_0=1.6306$ . Thus, from (22),

$$\frac{K_1(T)}{K_1(0)} \simeq (1 - 2.1 \times 10^{-3}T) \left(\frac{I}{I_0}\right)^3 = \left(1 - \frac{3T}{T_c}\right) \left(\frac{I}{I_0}\right)^3. \quad (23)$$

The above expression, as shown in Fig. 3, is in good agreement with the experimental values. A better comparison could be made if thermal expansion data were available over a wider temperature range.

#### Case of Nickel

The first anisotropy constant of nickel as a function of temperature decreases much more rapidly than that of iron and corresponds more nearly to a fiftieth power of the magnetization. (Frequently, it has been misstated as varying as the twentieth power.)

It is unlikely that this rapid decrease can be accounted for by the motion of the spins. *A priori*, it would seem that neighboring spins in nickel are correlated as in the case of iron. Such would lead to a tenth power law, with the additional dependence coming about because the coupling constants themselves are a function of temperature. One may write

$$K_1(T) = k_1(T) (I/I_0)^{10}, \quad (24)$$

where  $k_1$  is the anisotropy for parallel spins.

Equation (24) agrees reasonably well with experiment<sup>19</sup> (Fig. 4) if, as in cobalt,  $k_1$  has a linear dependence on temperature, i.e.,

$$k_1 = K_1(0) [1 - 1.74(T/T_c)]. \quad (25)$$

In particular, the positive part of  $K_1$  at high temperatures is reproduced by this type of expression. However, a theoretical reason for the postulate (25) is lacking.

Brenner<sup>9</sup> has shown that some linear dependence of  $K_1$  upon  $T$  should exist due to thermal expansion, but existing data show this effect in Ni is too small to account for (25).

The change in sign of  $K_1$  at  $T/T_c=0.6$ , which experimentally is still somewhat in doubt, is a key point toward understanding the anisotropy of nickel; for if it exists, the empirical relation of Brückhatov and Kirensky, which other authors have attempted to justify theoretically,<sup>8</sup> is ruled out. Although the positive

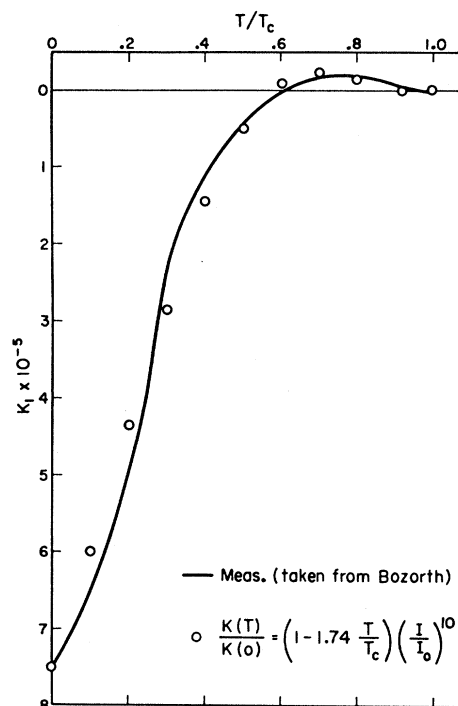


FIG. 4. The anisotropy of nickel. The measured values are taken from Bozorth (reference 19).

values of  $K_1$  are quite small, the magnitude of the positive coupling evidently is quite large; otherwise, no measurable anisotropy would appear at these high temperatures.

#### APPENDIX

The partition function for the whole crystal is given by

$$Z = \sum_n \exp\left(-\frac{(K_{0n} + K_{1n}s)}{kT}\right), \quad (26)$$

where  $K_{0n}$  is that part of the total energy of the  $n$ th eigenstate which is independent of the direction of the applied magnetic field  $H$ , and  $K_{1n}s$  is that part which has directional dependence. The symbol  $s$  is an abbreviation for  $\alpha_1^2\alpha_2^2 + \alpha_1^2\alpha_3^2 + \alpha_2^2\alpha_3^2$ , the  $\alpha$ 's being the direction cosines of  $H$  (or the bulk magnetization) with the crystal axes. [It is unnecessary in (26) to include states for which the bulk magnetization of that state is not aligned with the field, since measurements of anisotropy are made by extrapolating to infinite field.]

To obtain  $K_1$ , one expands the thermodynamic function for the free energy in powers of  $s$ ,

$$F = F_0 + \left(\frac{\partial F}{\partial s}\right)_{s=0} s + \dots, \quad (27)$$

and, by comparison with (1),

$$K_1(T) = \left(\frac{\partial F}{\partial s}\right)_{s=0}. \quad (28)$$

<sup>17</sup> *American Institute of Physics Handbook* (McGraw-Hill Book Company, Inc., New York, 1957), p. 4-54.

<sup>18</sup> E. A. Owen and D. M. Jones, *Proc. Phys. Soc. (London)* **B67**, 456 (1954).

<sup>19</sup> R. M. Bozorth, *Ferromagnetism* (D. Van Nostrand Company, Inc., Princeton, 1951), p. 569.

But statistically<sup>20</sup>  $F = -kT \ln Z$  and therefore, from (26) and (28),

$$K_1(T) = \sum_n \exp\left(-\frac{K_{0n}}{kT}\right) K_{1n} / \sum_n \exp\left(-\frac{K_{0n}}{kT}\right). \quad (29)$$

Upon making use of the ideas discussed in the text,

$$K_{0n} + K_{1n}(\alpha_1^2\alpha_2^2 + \alpha_1^2\alpha_3^2 + \alpha_2^2\alpha_3^2) = N\{k_{0n} + N^{-1}K_1(0)(\beta_{1n}^2\beta_{2n}^2 + \beta_{1n}^2\beta_{3n}^2 + \beta_{2n}^2\beta_{3n}^2)\}, \quad (30)$$

where  $k_{0n}$  and  $N^{-1}K_1(0)$  are appropriate to one of the

<sup>20</sup> In reality the Gibbs' free energy is desired, since measurements are made at constant pressure. However, the difference between measurements at constant strain and constant pressure is negligible for most materials.

$N$  atoms and the  $\beta$ 's refer to the local magnetization about that atom.

For each low-energy eigenstate  $n$ , one may picture the local magnetization as making an angle  $\Theta_n$  (defined by  $I_n/I_0$ ) with the field direction. Thus, in analogy with (5),

$$K_{1n} = K_1(0)P_4(\cos\Theta_n). \quad (31)$$

Finally, upon replacing sums by integrals, (29) goes over to

$$K_1(T) = K_1(0) \int f(\Theta)P_4(\cos\Theta)d\tau / \int f(\Theta)d\tau. \quad (32)$$

Zener assumed a random walk distribution function for  $f(\Theta)$ ; Brenner, a molecular field function.

## Low-Temperature Magnetic Studies of Uranium Hydride, Uranium Deuteride, and Uranium Dioxide

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A study of magnetization as a function of temperature and magnetic field has been carried out for uranium hydride, uranium deuteride, and uranium dioxide at temperatures from 300°K to 1.3°K and in magnetic fields from 60 000 gauss down to zero field. The apparent saturation magnetization for the samples of beta-uranium hydride used is  $1.18 \pm 0.03$  Bohr magnetons per atom of uranium and for one sample of uranium deuteride is  $0.98 \pm 0.03$  Bohr magneton per atom of uranium. The magnetic moment of uranium dioxide, limited by what may be antiferromagnetic ordering, is about 0.025 Bohr magneton per atom of uranium at 35 000 gauss and 1.3°K. This result makes possible corrections for the moments of  $UH_3$  and  $UD_3$  on the basis of a known oxygen content or an estimate of the oxide impurity on the basis of apparent saturation. A high zero-field remanent magnetization (over 50% of the saturation magnetization for a spherical sample) is observed, attesting to the pronounced magnetic hardness of beta-uranium hydride. Analytic expressions have been worked out for magnetization as a function of temperature for zero magnetic field and 11 500 gauss, leading to a paramagnetic  $\theta$  of 180°K and a ferromagnetic  $\theta$  of 168°K. An estimate of  $2 \times 10^6$  gauss is made for the molecular field in  $UO_2$ .

### INTRODUCTION

IN recent years, much interest has been shown in the overlap of wave functions as associated with exchange interactions, and how they foreshadow ferromagnetism and antiferromagnetism. The formerly conventional ferromagnetic and antiferromagnetic substances have been in the iron ( $3d$  unpaired electrons) group; also the rare earth group ( $4f$  unpaired electrons) has yielded ferromagnetic<sup>1</sup> and antiferromagnetic substances.<sup>2</sup> It is then of particular interest to study possible exchange interactions originating in  $5f$  and  $6d$  configurations in the actinide elements and their compounds. The discovery of a ferromagnetic transition in uranium hydride<sup>3</sup> at 173°K heightened the interest in the study of some of these interactions. Various low-field studies have been made of the magnetic

properties of beta-uranium hydride. The susceptibility above the Curie temperature was studied by Trzebiatowski, Stalinski, and Sliwa,<sup>3</sup> by Gruen,<sup>4</sup> and later by Lin and Kaufmann.<sup>5</sup> Estimates of 2.9 Bohr magnetons per atom<sup>4</sup> were made from the low-field susceptibility measurements, using

$$\mu = C[\chi(T + \Delta)]^{\frac{1}{2}}. \quad (1)$$

Here  $\mu$  is the intrinsic moment,  $\chi$  is the susceptibility,  $T$  the absolute temperature, and  $C$  and  $\Delta$  are constants. In the neighborhood of 173°K, there is a more rapid increase in the susceptibility. This, together with hysteresis and direct zero-field magnetization measurements,<sup>6</sup> confirmed the strong ferromagnetism of

<sup>3</sup> Trzebiatowski, Stalinski, and Sliwa, *Roczniki Chem.* **26**, 110 (1952); **28**, 12 (1954).

<sup>4</sup> D. M. Gruen, *J. Chem. Phys.* **23**, 1708 (1955).

<sup>5</sup> S. T. Lin and A. R. Kaufmann, *Phys. Rev.* **102**, 640 (1956).

<sup>6</sup> W. E. Henry and D. M. Gruen, *Phys. Rev.* **98**, 1200(A) (1955).

<sup>1</sup> Banister, Legvold, and Spedding, *Phys. Rev.* **94**, 1140 (1954); Elliott, Legvold, and Spedding, *Phys. Rev.* **94**, 1143 (1954).

<sup>2</sup> W. E. Henry, *Phys. Rev.* **98**, 226(A) (1955).