

$p_1=0.05$  are shown in Table IV along with the high- and low-temperature asymptotes for each stage. It should be noted that essentially 100% of the ions are accounted for in stages 2 and 3, and 96% in stage 4. Unfortunately, only 89% are accounted for in stage 1. There is no simple way to take this missing 11% into account in the calculation, but an upper limit to its contribution to the stage-1 lower asymptote can be established by taking all of it as situated in clusters of five spins locking into a configuration with spin  $S$  (the four-spin clusters are expected to lock into an  $S \cong 0$  configuration). This gives a variation in the low-temperature asymptote of about  $+0.022$ , representing a maximum variation of about  $+3.8\%$ .

In Fig. 7 we display the curve constructed under the assumptions that the 11% error in stage 1 contributes nothing to its low-temperature asymptote and that the concentration of ions for a given stage is best estimated by using the low-temperature asymptote from the previous stage. It is seen that the experimental data lie

above the curve for fourth nn, but below that for second nn, and that the slope is higher than the slope of either. While the range of the data is not sufficient to fix any interactions firmly, we can conclude that (1) the observed variation in  $X(\tau)$  can be accounted for using second-, third-, and fourth-nn interactions; (2) the strengths of these interactions are of the same order of magnitude, and (3) the interaction strength is of the order of magnitude of  $0.1^\circ\text{K}$ .

While more elaborate calculations could be carried out, e.g., taking  $R_2=R_3=R_4$  and calculating the curve for interactions among these 26 ions, they hardly seem profitable with the limited data available. It would be highly desirable to have available measurements over several decades of temperature.

#### ACKNOWLEDGMENTS

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### Variation of Magnetocrystalline Anisotropy of Iron with Field and Temperature

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The magnetocrystalline anisotropy constant  $K_1$  of iron was determined from static torque measurements on a {001} single-crystal disk at fields between 3000 and 18 000 Oe, and at temperatures between 77 and 900°K. It was found that (i)  $(\partial K_1/\partial T)/K_1 \cong 10(\partial M/\partial T)/M$  above 300°K, in agreement with Zener; (ii)  $(\partial K_1/\partial H)/K_1 \cong 22(\partial M/\partial H)/M$  below 600°K, and at  $H \cong 10$  KOe; and (iii)  $(\partial K_1/\partial H)/(\partial K_1/\partial T) \cong -1.25 \times 10^{-3}$  °K/Oe over the whole temperature range of this investigation.

#### INTRODUCTION

THE anisotropic part of the magnetocrystalline free-energy density of a cubic crystal may be written as

$$F = K_1(\alpha_1^2\alpha_2^2 + \alpha_2^2\alpha_3^2 + \alpha_3^2\alpha_1^2) + K_2\alpha_1^2\alpha_2^2\alpha_3^2 + \dots,$$

where the  $\alpha$ 's are the direction cosines of the magnetization with respect to the cubic axes, and the  $K$ 's are usually considered to be characteristic of the material and to depend on temperature only.

For iron few  $K$  data seem to be available. Values of  $K_1$  and  $K_2$  were derived by Bozorth<sup>1</sup> from magnetization curves measured earlier by Honda *et al.*<sup>2</sup> These data cover almost the whole ferromagnetic temperature range. They may, however, not be very accurate with regard to the rather indirect method of determination.

<sup>1</sup> R. M. Bozorth, *J. Appl. Phys.* **8**, 575 (1937).

<sup>2</sup> K. Honda, H. Masumoto, and S. Kaya, *Sci. Rept. Tohoku Univ.* **17**, 111 (1928).

More recent torque measurements by Bozorth,<sup>3</sup> by Hall,<sup>4</sup> and by Graham<sup>5</sup> have been carried out up to 575°K.

These  $K$  values were, as usual, obtained by extrapolation to infinite field using  $H^{-1}$  or  $H^{-1/2}$  plots.<sup>5</sup> Such an extrapolation is based on the assumption that the measured isothermal variation of  $K$  with field is exclusively due to incomplete alignment of the equilibrium spontaneous magnetization  $M_s(T)$  at the temperature of the measurement. Experimental results supporting this aspect were presented by Kouvel and Graham.<sup>6</sup>

On the other hand, it is positively known from

<sup>3</sup> R. M. Bozorth, *American Institute of Physics Handbook*, edited by D. E. Gray (McGraw-Hill Book Company, Inc., New York, 1957), p. 5-221.

<sup>4</sup> R. C. Hall, *J. Appl. Phys.* **30**, 816 (1959).

<sup>5</sup> C. D. Graham, Jr., *Phys. Rev.* **112**, 1117 (1958); *J. Appl. Phys. Suppl.* **30**, 317S (1959); *ibid.* **31**, 150S (1960).

<sup>6</sup> J. S. Kouvel and C. D. Graham, *J. Appl. Phys.* **28**, 340 (1957).

TABLE I. Magnetocrystalline anisotropy coefficient  $K_1(0, T)$  of iron.

From $K_1$ versus $H$		From $H$ versus $T$	
$K_1(0, T)$ in $10^3$ ergs $\text{cm}^{-3}$	$T$ in $^\circ\text{K}$	$K_1(0, T)$ in $10^3$ ergs $\text{cm}^{-3}$	$T$ in $^\circ\text{K}$
515±6	77	502	166–20
489±6	200	460	275± 5
450±5	293	450	292± 5
394±5	373	399	365± 2
307±4	473	348	425± 2
210±3	573	298	481± 2
123±2	673	248	530± 2
58±2	773	198	583± 2
21±1	873	148	640± 2
		98	708± 2
		49	794± 2
		29.3	847± 2
		19.5	879± 2
		9.7	921± 2

magnetocaloric investigations,<sup>7–10</sup> and it may rather safely be also concluded from measurements of the field dependence of magnetization at very high fields (paraprocess, see Weiss and Forrer<sup>11</sup> for nickel, Danan<sup>12</sup> for iron and nickel) that in an applied field the intrinsic magnetization is increased beyond its equilibrium value  $M_s(T)$ . The paraprocess was theoretically treated by Holstein and Primakoff.<sup>13</sup> From these facts and from theoretical work of Zener<sup>14</sup> and Van Vleck<sup>15</sup> relating the temperature variation of the anisotropy  $K$  to the intrinsic magnetization, it was first concluded by Veerman *et al.*<sup>16</sup> that there may also be a nontrivial variation of  $K$  with field being related to the paraprocess, and that hence  $K$  may be a single-valued function  $K[M(H, T)]$  of the intrinsic magnetization with respect to variations of  $T$  and  $H$ . Corresponding experiments on nickel<sup>16,17</sup> and on gadolinium<sup>18</sup> appear to support this view, at least within limited ranges of temperatures.

In this work,  $K_1(H, T)$  of iron has been determined from static torque measurements at fields between 3000 and 18 000 Oe, and at temperatures between 77 and 900°K. The work is meant (i) to supply accurate data for  $K_1$  over a larger temperature range, and (ii) to see what relations exist between  $K_1$  and the magnetization  $M$ .

<sup>7</sup> E. C. Stoner, *Rev. Mod. Phys.* **25**, 2 (1953).

<sup>8</sup> T. Okamura, *Sci. Rept. Tohoku Univ.* **24**, 745 (1935).

<sup>9</sup> L. F. Bates and J. C. Weston, *Proc. Phys. Soc. (London)* **53**, 5 (1941).

<sup>10</sup> L. F. Bates and D. R. Healey, *Proc. Phys. Soc. (London)* **55**, 188 (1943).

<sup>11</sup> P. Weiss and R. Forrer, *Ann. Phys. (Paris)* **5**, 153 (1926).

<sup>12</sup> H. Danan, *Compt. Rend.* **246**, 73, 401 (1958).

<sup>13</sup> T. Holstein and H. Primakoff, *Phys. Rev.* **58**, 1098 (1940).

<sup>14</sup> C. Zener, *Phys. Rev.* **96**, 1335 (1954).

<sup>15</sup> J. H. Van Vleck, *J. Phys. Radium* **20**, 124 (1959).

<sup>16</sup> J. Veerman, J. J. M. Franse, and G. W. Rathenau, *J. Phys. Chem. Solids* **24**, 947 (1963).

<sup>17</sup> J. Veerman and G. W. Rathenau, in *Proceedings of the International Conference on Magnetism, Nottingham* (The Institute of Physics and the Physical Society, London, 1965), p. 737.

<sup>18</sup> C. D. Graham, Jr., in *Proceedings of the International Conference on Magnetism, Nottingham* (The Institute of Physics and The Physical Society, London, 1964), p. 740.

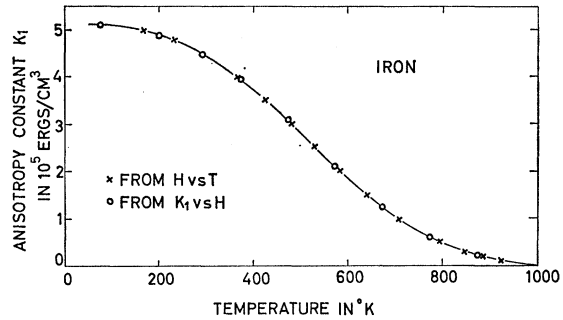


FIG. 1. Temperature dependence of the magnetocrystalline anisotropy coefficient  $K_1(0, T)$  of iron.

## EXPERIMENTS AND RESULTS

The work is limited to measurements of the coefficient  $K_1$  from torque curves in a  $\{001\}$  plane. Here the anisotropic part of the magnetocrystalline free-energy density of a cubic crystal reduces to  $F = -(\frac{1}{8}K_1)\cos 4\theta$ , where  $\theta$  is the angle between a  $\langle 100 \rangle$  direction in the plane of measurement and the magnetization direction.

The sample is a zone melted iron single crystal<sup>19</sup> disk with 3.17 mm diam and 0.22 mm thickness, cut with its planes parallel to a  $\{001\}$  crystal plane. After careful mechanical finishing the disk was electrolytically polished. The polishing not only served to obtain a stress-free surface, but also to round off the sharp edges of the disk where otherwise the magnetization may resist alignment with field up to rather high fields.<sup>6</sup> The volume of the sample was determined from its weight, taking the known density of pure iron. At temperatures above and below room temperature the volume was corrected for thermal expansion. At low and high temperatures the complete torque balance system including the sample was kept in a vacuum of  $10^{-3}$  Torr in order to prevent condensation of various vapors on parts

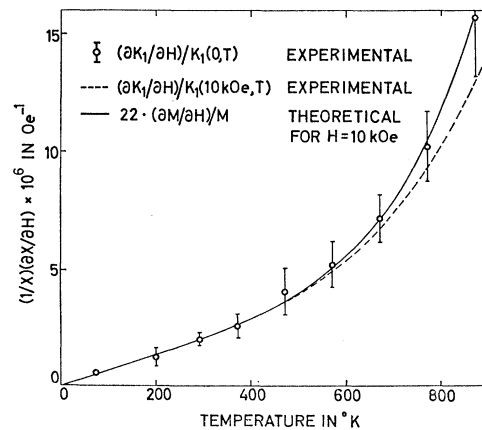


FIG. 2. Temperature dependence of  $(\partial K_1/\partial H)/K_1$  as determined experimentally in this work, and of  $(\partial M/\partial H)/M$  as calculated after Holstein and Primakoff (Ref. 13) for  $H=10$  000 Oe.

<sup>19</sup> The crystal was kindly given to us by Dr. H. Thomas of the Vacuumschmelze A. G., Hanau, Germany.

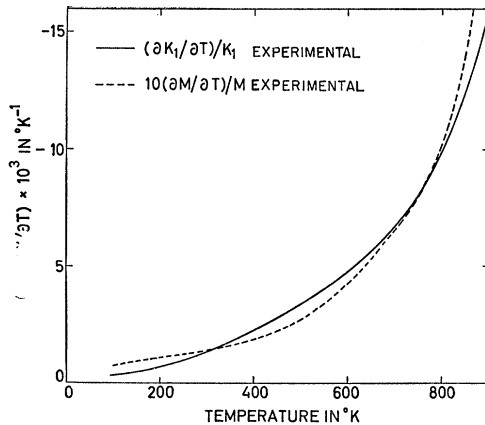


FIG. 3. Temperature dependence of  $(\partial K_1/\partial T)/K_1$  as determined in this work, and of  $(\partial M/\partial T)/M$  from data given by Potter (Ref. 20).

of the balance, or oxidation of the sample, respectively. The torque balance was calibrated with a 25% Fe, 75% Ni alloy wire, 0.1 mm thick and 5 mm long, in the disordered state, i.e., as quenched from 1000°K. At this composition  $K_1 \approx 0$  in the disordered alloy.<sup>20</sup> Hence the wire has practically shape anisotropy only, which may be calculated fairly accurately.

From the experimental data  $K_1(H, T)$  two sets of curves were drawn:  $K_1$  versus  $H$  at constant  $T$ , and  $H$  versus  $T$  at constant  $K_1$ . Both kinds of curves appear to become very exactly linear (within the relative accuracy of the measurements, i.e.,  $\sim 1\%$ ) at high enough fields, depending on temperature ( $H > 4000$  Oe at 900°K,  $H > 14\,000$  Oe at 77°K). Linear extrapolation of such a linear curve section towards  $H = 0$  yields in the case of a  $K-H$  curve a  $K_1(0, T)$  value corresponding to the temperature kept constant along the curve, and in the case of a  $H-T$  curve a temperature  $T$  corresponding to the  $K_1(0, T)$  value kept constant along the curve. Corresponding values of  $K_1$  and  $T$  thus determined are given in Table I and are plotted in Fig. 1. Accordingly, both methods, which correspond to the methods to determine the spontaneous magnetization as introduced by Weiss and Forrer,<sup>11</sup> lead to identical results within the relative accuracy of the measurements. This appears to be a nontrivial result. It is thus suggested that in quoting magnetocrystalline anisotropy data, either  $K_1(H, T)$  should be given at given fields  $H$  (see Veerman *et al.*<sup>16,17</sup>), or instead  $K_1(0, T)$  as extrapolated to zero field, plus the slope  $(\partial K_1/\partial H)_T$  and the field range used for extrapolation. It may be mentioned that extrapolation of our results  $K_1(H, T)$  over  $H^{-1}$

<sup>20</sup> R. M. Bozorth and J. G. Walker, Phys. Rev. **89**, 624 (1953).

towards infinite field yields, within the accuracy of the measurements, the  $K_1$  values given by Bozorth<sup>3</sup> and by Graham<sup>5</sup> at temperatures between 77°K and 575°K.

The slope  $(\partial K_1/\partial H)_T$  of the linear part of the  $K_1-H$  curves was found to be a function of temperature. In Fig. 2 the relative slope  $(\partial K_1/\partial H)/K_1(0, T)$  for iron is given as a function of temperature. At room temperature for iron  $(1/K_1)(\partial K_1/\partial H) \approx 2 \times 10^{-6}$  Oe<sup>-1</sup> to be compared to Veerman's value  $5.3 \times 10^{-6}$  Oe<sup>-1</sup> for nickel.

### RELATIONS BETWEEN $K_1$ AND $M$

According to Zener's theory<sup>14</sup>

$$(1/K_1)(\partial K_1/\partial T) = m_T(1/M)(\partial M/\partial T), \quad (1)$$

or equivalently  $K_1(T)/K_1(0) = [M(T)/M(0)]^{m_T}$ , with  $m_T = 10$  for cubic crystals. This relation is shown in Fig. 3 to hold fairly well at room temperature and above, taking  $K_1 \equiv K_1(0, T)$ , and using  $M(T)/M(0)$  values as given by Potter.<sup>21</sup> At temperatures below room temperature  $m_T = 3$  to 6, in fair agreement with results of Bozorth<sup>3</sup> and Graham<sup>5</sup> (see Graham<sup>5</sup>). For nickel Veerman *et al.*<sup>16</sup> found  $m_T = 26$  at 288°K.

According to Veerman *et al.*,<sup>16,17</sup> a relation of the form

$$(1/K_1)(\partial K_1/\partial H) = m_H(1/M)(\partial M/\partial H) \quad (2)$$

was experimentally found for nickel to hold between 150 and 300°K, with  $m_H \approx 25$ . Hence, at room temperature  $m_H \approx m_T$ , whence Veerman *et al.* concluded that  $K_1$  is a single-valued function  $K_1[M(H, T)]$  of the magnetization with respect to variations of the parameters  $H$  and  $T$ . For iron, experimental values of  $\partial M/\partial H$  are available only at room temperature<sup>12,22</sup> and below,<sup>22</sup> and at fields above 4000 Oe. These experimental values seem to agree reasonably well with theoretical values calculated after Holstein and Primakoff.<sup>13</sup> Therefore, in Fig. 2  $(1/M)(\partial M/\partial H)$  thus calculated for  $H = 10\,000$  Oe is compared with  $(1/K_1)(\partial K_1/\partial H)$  as measured at 10 000 Oe. It is seen that Eq. (2) holds very well for temperatures below  $\sim 600$ °K, i.e., below about one half of the Curie temperature, with  $m_H \approx 22 = 2.2m_T$ . This does, not however, necessarily exclude the possibility that for iron,  $K_1$  is a single-valued functions of the intrinsic magnetization  $M(H, T)$  within a certain temperature range, because the absolute values of the available data for  $\partial M/\partial H$  do not seem to be sufficiently reliable.

Finally it may be mentioned that experimentally

$$(\partial K_1/\partial H)/(\partial K_1/\partial T) \approx -1.25 \times 10^{-3} \text{ } ^\circ\text{K Oe}^{-1} \quad (3)$$

over the whole temperature range of this investigation.

<sup>21</sup> H. H. Potter, Proc. Roy. Soc. (London) **A146**, 362 (1934).

<sup>22</sup> D. Ehlermann, thesis, Stuttgart, 1965 (unpublished).