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**5f-8. Gyromagnetic Ratios and Spectroscopic Splitting Factors.** The magneto-mechanical ratio  $g'$  is defined by the relation

$$g' = \frac{M}{J} \frac{2mc}{e}$$

where  $m/e$  is the mass-to-charge ratio of the electron and  $c$  is the velocity of light.  $M/J$  is the ratio of the magnetic moment to the angular momentum of the electrons which contribute to the spontaneous magnetization as measured in an Einstein-de Haas or a Barnett-effect experiment (Sec. 5f-1).

The spectroscopic splitting factor  $g$  for ferromagnetic materials is defined as:

$$g = \frac{h\nu}{\mu_B H}$$

where  $\nu$  is the Larmor precession frequency of the moment associated with a sample of the material in a field  $H$  as measured in a ferromagnetic-resonance experiment,  $h$  is Planck's constant, and  $\mu_B$  is the Bohr magneton. See Table 5f-16.

The Kittel-Van Vleck relation between  $g$  and  $g'$  is usually written

$$1/g + 1/g' = 1$$

which reduces to  $g = g' = 2$  when  $g$  and  $g'$  are equal. When  $g$  and  $g'$  differ considerably it has been proposed<sup>1</sup> that the relation is

$$g' = g/(g - \rho)$$

where  $\rho$  may be calculated from atomic structure when this is sufficiently well known. In some cases  $g'$  may then be negative.

TABLE 5f-16. VALUES OF  $g$  AND  $g'$

Material	$g'$ (obs) [1]	$g$ (calc)	$g$ (obs)†	Material [3]	$g'$ (obs)	$g$ (calc)
Fe.....	1.919	2.09	2.09 [2]	Nd <sub>2</sub> O <sub>3</sub> .....	0.77	3.3
Co.....	1.850	2.18	2.18 [2]	Gd <sub>2</sub> O <sub>3</sub> .....	2.12	1.9
Ni.....	1.837	2.19	2.19 [2]	Dy <sub>2</sub> O <sub>3</sub> .....	1.29	4.5
FeNi‡.....	1.908	2.10	2.10 [2]	Eu <sub>2</sub> O <sub>3</sub> .....	> 4.5	< 1.3
CoNi‡.....	1.846	2.18	2.17 [2]	CrCl <sub>3</sub> .....	1.95	2.1
Cu <sub>2</sub> MnAl.....	1.993	2.01	2.01 [4]	MnCO <sub>3</sub> .....	2.00	2.0
MnSb.....	1.978	2.02		MnSO <sub>4</sub> .....	2.29	1.8
NiFe <sub>2</sub> O <sub>4</sub> .....	1.849	2.18	2.20 [5]	FeSO <sub>4</sub> .....	1.89	2.1
Fe-Ni-Mo§.....	1.905	2.10	2.10 [6]	CoCl <sub>2</sub> .....	1.45	3.2
FeS <sub>1.2</sub> .....	1.9	2.1		CoSO <sub>4</sub> .....	1.57	2.8

Probable errors in  $g'$  are usually 0.002 to 0.004 in the metals, and several percent in the nonmetals.

† No values of  $g$ (obs) available for Nd<sub>2</sub>O<sub>3</sub> to CoSO<sub>4</sub>.

‡ Other compositions of alloys are given by Scott [1] and Asch [2].

§ Supermalloy: 17 Fe, 78 Ni, 5 Mo. (wt. %).

In solid solutions of composition  $A_xB_{1-x}$ ,  $g'$  is observed<sup>1</sup> to follow the relation

$$\frac{x + k(1-x)}{x/g_1' + k(1-x)/g_2'}$$

$k$  being an empirical constant.

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**5f-9. Change of Curie Point and Néel Point with Pressure.** A hydrostatic pressure changes the Curie Point or Néel Point of magnetic materials, usually from about +5 K to -5 K per kilobar (987 atmospheres). See Table 5f-17.

<sup>1</sup> See Ref. 7 for Table 5f-16.

TABLE 5f-17. EFFECT OF PRESSURE ON CURIE AND NÉEL TEMPERATURES<sup>a,b</sup>

Substance	$dT/dP$ , K/kbar	Ref.	Substance	$dT/dP$ , K/kbar	Ref.
Au <sub>2</sub> Mn.....	AF 0.47	1	Ni <sub>0.5</sub> Zn <sub>0.5</sub> Fe <sub>2</sub> O <sub>4</sub> ...	FM 0.99	40
Au <sub>4</sub> Mn.....	AF 2.7	2-4	Ni <sub>0.5</sub> Zn <sub>0.2</sub> Fe <sub>2</sub> O <sub>4</sub> ...	FM 0.73	40
Ba <sub>0.1</sub> Sr <sub>0.9</sub> RuO <sub>3</sub> ...	FM -0.56	5	NiFe <sub>2</sub> O <sub>4</sub> .....	FM 1.16	40
CaCrO <sub>3</sub> .....	FM -0.23	6	Fe <sub>0.7</sub> Mn <sub>0.3</sub> .....	AF -2.5	45
CaMnO <sub>3</sub> .....	FM 0.41	5	Fe <sub>0.70</sub> Ni <sub>0.30</sub> .....	FM -5.8	9, 46
Ca <sub>0.25</sub> La <sub>0.75</sub> MnO <sub>3</sub> ...	FM 1.07	7	Fe <sub>0.64</sub> Ni <sub>0.36</sub> .....	FM -4 <sup>c</sup>	9, 39
Ca <sub>0.85</sub> Sr <sub>0.15</sub> MnO <sub>3</sub> ...	FM 0.44	7a	Fe <sub>0.32</sub> Ni <sub>0.68</sub> .....	FM -0.1	47, 47a
Ca <sub>0.75</sub> Sr <sub>0.25</sub> MnO <sub>3</sub> ...	FM 0.38	7a	Fe <sub>0.47</sub> Rh <sub>0.53</sub> .....	FM 5.1	9
Ca <sub>0.5</sub> Sr <sub>0.5</sub> MnO <sub>3</sub> ...	FM 0.55	7a	Fe <sub>0.96</sub> Si <sub>0.04</sub> .....	FM -0.1	1
CdCr <sub>2</sub> S <sub>4</sub> .....	FM -0.58	8	Fe <sub>0.90</sub> Si <sub>0.10</sub> .....	FM 0.2	9
CdCr <sub>2</sub> Se <sub>4</sub> .....	FM -0.84	8, 5	Gd.....	FM -1.4	1, 9, 23
Co.....	FM 0.0	9, 10			27, 30
CoCO <sub>3</sub> .....	FM 0.1	11			48
CoF <sub>2</sub> .....	AF 0.0	12		1.2 to 1.6 <sup>c</sup>	49, 50
CoO.....	AF 0.60	13, 13a,	GdN.....	FM 0.08	51
		13b	HgCr <sub>2</sub> S <sub>4</sub> .....	FM 0.14	8
CoS <sub>2</sub> .....	FM -0.64	5	HgCr <sub>2</sub> Se <sub>4</sub> .....	FM -0.95	8
Cr.....	AF -5.1 <sup>d</sup>	14, 15	Ho.....	AF -0.4	1, 27
	-5 to -6 <sup>c</sup>	16, 17			32
Cr <sub>2</sub> O <sub>3</sub> .....	AF -1.6	18		-0.3 to -0.5 <sup>c</sup>	52
CrN.....	AF 0.85	18a	La <sub>0.75</sub> Sr <sub>0.25</sub> MnO <sub>3</sub> ...	FM 0.6	9
CrSi <sub>1.17</sub> .....	FM -2.6	19	$\gamma$ Mn <sub>0.95</sub> Cu <sub>0.05</sub> .....	AF -3.5	52a
CrTe.....	FM -5.6	20, 21	MnAs.....	FM -12 <sup>e</sup>	53, 54
Cr <sub>3</sub> Te <sub>4</sub> .....	FM -7.35	21a			55
CsNiF <sub>3</sub> .....	FM 0.53	22		AF 2.2	50
CuCr <sub>2</sub> S <sub>4</sub> .....	FM -1.39	5	MnBi.....	FM -0.7	55
CuCr <sub>2</sub> Se <sub>4</sub> .....	FM -0.44	5	MnCO <sub>3</sub> .....	FM 0.4	11
Dy.....	AF -0.4	1, 23	Mn <sub>1.2</sub> In <sub>0.8</sub> Cu <sub>2</sub> .....	AF 1.5 <sup>f</sup>	2
		24, 25	MnFe.....	AF 0.3	57, 12
	-0.3 to -0.6 <sup>c</sup>	26, 27		0.3 to 0.7 <sup>c</sup>	
		28, 29	Mn <sub>3</sub> Ge <sub>3</sub> .....	FM 0.42	57a
Dy.....	FM -1.25	30	MnO.....	AF 0.3	58
Dy <sub>0.58</sub> Gd <sub>0.42</sub> .....	AF -0.85	31	MnP.....	FM -1.4	59, 60
	FM -1.01		MnS.....	AF 1.20	60a
Er.....	AF -0.25	24, 32	MnSb.....	FM -3	55, 20
	FM -0.8		MnTe.....	AF 2	61, 62
ErCo <sub>3</sub> .....	FM -4.17	32a	MnTe <sub>2</sub> .....	AF 0.2	63
Eu.....	AF 0.45	33, 34,	Ni.....	FM 0.32	1, 9, 64
		34a	Alumel-94 Ni....	FM 0.04	9
	0 to 0.9 <sup>c</sup>		Monel.....	FM 0.07	9
EuO.....	FM 0.4	34, 35	Ni <sub>0.80</sub> Cu <sub>0.20</sub> .....	FM 0.14	1
		36	Ni <sub>0.70</sub> Cu <sub>0.30</sub> .....	FM 0.05	1
EuS.....	FM 0.28	37	NiS.....	AF -6.0	65
EuSe.....	AF 0.0	38	Ni <sub>0.93</sub> Si <sub>0.07</sub> .....	FM 0.16	1
EuTe.....	AF 0.0	38	Ni <sub>0.91</sub> Si <sub>0.09</sub> .....	FM 0.05	1
Fe.....	FM 0.0	9, 39	Pd <sub>0.95</sub> Co <sub>0.05</sub> .....	FM 0.1	65a
FeO.....	AF 0.65	13a	Pd <sub>0.997</sub> Fe <sub>0.003</sub> .....	FM -0.004	66
<i>Garnets</i>			Pd <sub>0.97</sub> Fe <sub>0.03</sub> .....	FM -0.1	66
Gd <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub> .....	FM 1.28	13	RbFeCl <sub>3</sub> .....	FM 2.13	66a
Gd <sub>3</sub> AlFe <sub>4</sub> O <sub>12</sub> .....	FM 0.58	40	RbNiF <sub>3</sub> .....	FM 0.6	67
Tb <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub> .....	FM 1.23	13	Sc <sub>3</sub> In.....	FM 0.2	68
Dy <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub> .....	FM 1.15	13	SrRuO <sub>3</sub> .....	FM -0.63	5
Er <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub> .....	FM 1.22	13	Tb.....	AF -0.8	1, 23
Yb <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub> .....	FM 1.08	13		-0.76 to -1.1 <sup>c</sup>	26, 27
Y <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub> .....	FM 1.25	13		FM -1.2	52, 69
Y <sub>1.5</sub> Gd <sub>1.5</sub> Fe <sub>4.5</sub> -				-1.06 to -1.24 <sup>c</sup>	70
Al <sub>0.5</sub> O <sub>12</sub> .....	FM 1.00	40	Tb <sub>0.7</sub> Y <sub>0.3</sub> .....	AF -0.5	27
<i>Spinel</i>			Tb <sub>0.3</sub> Y <sub>0.7</sub> .....	AF -0.3	27
Fe <sub>3</sub> O <sub>4</sub> .....	FM ~0	41	V <sub>2</sub> O <sub>3</sub> .....	AF -3.78	71
Mn <sub>0.5</sub> Zn <sub>0.5</sub> Fe <sub>2</sub> O <sub>4</sub> ...	FM 0.9	9, 42	YCrO <sub>3</sub> .....	AF 0.38	5
Ni <sub>0.3</sub> Zn <sub>0.7</sub> Fe <sub>2</sub> O <sub>4</sub> ...	FM 0.83	40, 43	ZrZn <sub>2</sub> .....	FM -1.2	72
		44			

\* Compiled by D. B. McWhan, Bell Telephone Laboratories.

<sup>a</sup> AF—antiferromagnetic. FM—ferro or ferrimagnetic.<sup>b</sup> 1 kbar  $\approx$  987 atm  $\approx$  1,020 kg/cm<sup>2</sup>.<sup>c</sup> Range of published values.<sup>d</sup>  $T_N(V) = T_N(V_0) \exp(-26.5 \Delta V/V_0)$ ; see McWhan and Rice [14].<sup>e</sup> Low-pressure phase FM; high-pressure phase AF.<sup>f</sup> Heusler alloys: for series of alloys see Austin and Mishra [30].

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**5f-10. Magnetic Anisotropy.**<sup>1</sup> The magnetocrystalline anisotropy energy density  $E_K$  can be expanded in powers of the magnetization ( $\mathbf{M}$ ) components. Since  $\mathbf{M}$  changes sign under time reversal, this expansion must contain only even<sup>2</sup> functions of the components of  $\mathbf{M}$ . In addition, the number of terms in the expansion may be reduced by the requirement that  $E_K$  be invariant under the crystallographic symmetry operations. An equivalent phenomenological description of  $E_K$  can be obtained by expanding it in powers of the direction cosines of  $\mathbf{M}$  with respect to the principal crystallographic axes.<sup>3</sup> Thus for cubic crystals, the anisotropy energy per unit volume is

$$E_K = K_1(\alpha_1^2\alpha_2^2 + \alpha_2^2\alpha_3^2 + \alpha_1^2\alpha_3^2) + K_2\alpha_1^2\alpha_2^2\alpha_3^2 + K_3(\alpha_1^4\alpha_2^4 + \alpha_2^4\alpha_3^4 + \alpha_1^4\alpha_3^4) + \dots$$

where the  $\alpha$ 's are the direction cosines of  $\mathbf{M}$  with respect to the cubic axes. Usually  $|K_2|$  is considerably smaller than  $|K_1|$ .

In hexagonal crystals,

$$E_K = K_1 \sin^2 \theta + K_2 \sin^4 \theta + K_3 \sin^6 \theta + K_4 \sin^6 \theta \cos 6\psi + \dots$$

where  $\theta$  is the polar angle of  $M$  with respect to the crystallographic  $c$  axis, and  $\psi$  is the azimuthal angle of  $M$  with respect to the  $a$  axis.

For tetragonal crystals,

$$E_K = K_1 \sin^2 \theta + K_2 \sin^4 \theta + K_3 \sin^4 \theta \sin^2 \psi \cos^2 \psi + \dots$$

where  $\theta$  and  $\psi$  are defined as in the hexagonal case.

To obtain the angular dependence of the anisotropy energy for each of the 32 crystal classes the functions of the direction cosines of  $M$  tabulated by Döring<sup>4</sup> must be corrected<sup>5</sup> in order to satisfy the requirement of time-reversal invariance. This means omitting all terms which are of odd degree in the direction cosines.

*Induced Anisotropy.* Induced anisotropy is a nonintrinsic anisotropy which is produced by some external treatment, for example, by cold working or by annealing in a magnetic field or in the presence of an applied mechanical stress. The axes of such anisotropies do not, in general, correspond to principal crystallographic axes but are related to the directions of cold working, applied magnetic field, or applied mechanical stress. The induced anisotropy energy resulting from magnetic anneal is of the form<sup>6</sup>

$$E_{K_i} = -F(\alpha_1^2\alpha_1'^2 + \alpha_2^2\alpha_2'^2 + \alpha_3^2\alpha_3'^2) - G(\alpha_1\alpha_2\alpha_1'\alpha_2' + \alpha_2\alpha_3\alpha_2'\alpha_3' + \alpha_1\alpha_3\alpha_1'\alpha_3') \dots$$

where  $\alpha_1, \alpha_2, \alpha_3$  are the direction cosines of  $\mathbf{M}$  with respect to the principal crystallographic axes and  $\alpha_1', \alpha_2', \alpha_3'$  are the direction cosines of  $\mathbf{M}$  with respect to the crystallographic axes at the time of the anneal.

<sup>1</sup> Compiled by V. J. Folen, Naval Research Laboratory.

<sup>2</sup> Except in cases where unidirectional anisotropy exists, as, for example, in Co-CoO interface materials. See W. H. Meiklejohn and C. P. Bean, *Phys. Rev.* **102**, 1413 (1956).

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TABLE 5f-18. MAGNETOCRYSTALLINE ANISOTROPY CONSTANTS OF SOME  
CUBIC METALS [1]  
(in ergs/cm<sup>3</sup>)

Material*	10 <sup>-4</sup> K <sub>1</sub>	10 <sup>-4</sup> K <sub>2</sub>	Material*	10 <sup>-4</sup> K <sub>1</sub>	10 <sup>-4</sup> K <sub>2</sub>
Fe [2] (Fig. 5f-30)	45	20	13.5 % Si-Fe.....	6 [11]	
Fe [3].....	48	0 ± 5	7 % Al-Fe†.....	45 [12]	
Fe [4].....	45	-3.5	16 % Al-Fe†.....	28 [12]	
77 K.....	52 [3]	~9.5 [5]	27 % Al-Fe†		
Ni (Fig. 5f-31)...	-5 [4, 6]	-2 [6]	Disordered....	-1 [12]	
77 K.....	-58 [6]	-21 [4,6]	Ordered.....	-12 [12]	
Fe-Ni (Fig. 5f-32).....			13 % Cu-Ni.....	-2.3 [13]	
30 % Fe-Co.....	10.2 [7]	16.0 [7]	24 % Cu-Ni.....	-0.5 [13]	
50 % Fe-Co.....	-7 [7]	-39 [7]	1.47 % Cr-Ni†....	-1.1 [14]	
70 % Fe-Co.....	-43 [7]	+5 [7]	77 K.....	-27 [14]	
65 % Co-Ni.....	-26 [8]	15 [8]	4.08 % Cr-Ni†....	0 [14]	
20 % Co-Ni.....	-0.4 [8]	0.8 [8]	77 K.....	-6.5 [14]	
25 % Fe, 25 % Co,			1.28 % V-Ni†....	-2.4 [14]	
50 % Ni.....	0.35 [9]	1.6 [9]	77 K.....	-36 [14]	
50 % Fe, 10 % Co,			3.93 % V-Ni†....	-0.28 [14]	
40 % Ni.....	6 [9]	16 [9]	77 K.....	-0.13 [14]	
10 % Fe, 40 % Co,			2 % Mo, 19 % Fe,		
50 % Ni.....	-7 [9]	-0.4 [9]	79 % Ni		
75 % Ni-Mn.....	3.3 [15]	-7 [15]	Quenched.....	-0.14 [16]	
77 K.....	5 [15]		Annealed.....	-0.33 [16]	
3.1 % Si-Fe.....	36.5 [10]		6 % Mo, 15 % Fe,		
5.1 % Si-Fe.....	28.5 [10]	-5 ± 5 [10]	79 % Ni		
7.5 % Si-Fe.....	17 [11]		Quenched.....	0.53 [16]	
			Annealed.....	0.77 [16]	

\* All percentages are in weight percent except those indicated by †.

#### References for Table 5f-18

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TABLE 5f-19. MAGNETOCRYSTALLINE ANISOTROPY CONSTANTS  
OF SOME CUBIC OXIDES AND OTHER CUBIC MATERIALS [1]  
(in ergs/cm<sup>3</sup>)

Material	$10^{-4}K_1$	$10^{-4}K_2$
Y <sub>2</sub> Fe <sub>5</sub> O <sub>12</sub> (YIG) [2*]	-0.4	
4.2 K	-2.45	
Y <sub>3</sub> Ga <sub>1.47</sub> Fe <sub>3.53</sub> O <sub>12</sub> [3*]	0	
0 K	-1.2	
Y <sub>3</sub> In <sub>0.20</sub> Fe <sub>4.80</sub> O <sub>12</sub> [4]	-0.4	
4.2 K	-2.4	
Y <sub>3</sub> Sc <sub>0.87</sub> Fe <sub>4.13</sub> O <sub>12</sub> [4]	~-0.1	
4.2 K	-1.0	
Y <sub>2.52</sub> La <sub>0.38</sub> Fe <sub>5</sub> O <sub>12</sub> [5*]	$K_1/M = -380e$	
88 K	$K_1/M = -1080e$	
Gd <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub> [2*,6]	0	
4.2 K	-22	
Er <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub> [6]	-0.6	
100 K	-2.2	
Yb <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub> [7]	-0.8	
1.5 K	-900	900
Tb <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub> [6]	-1	
80 K	-76	-760
Ho <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub> [6]	~0	
80 K	-80	-27
Dy <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub> [6]	~0	
80 K	-97	21.4
Sm <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub> [6]	-2	
80 K	-120	100
Eu <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub> [8*]	-0.4	0
170 K	-2	1
Tm <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub> [9*]	-1.1	~0
77 K	21	10
MnFe <sub>2</sub> O <sub>4</sub> [10]	-4	
92 K [11]	-19.1	-2.15
Mn <sub>0.75</sub> Fe <sub>2.25</sub> O <sub>4</sub> [12]	0.9	
90 K	0	-9
Mn <sub>0.50</sub> Fe <sub>2.50</sub> O <sub>4</sub> [12]	-1.6	
90 K	-10.7	
Mn <sub>0.53</sub> Mg <sub>0.75</sub> Fe <sub>1.71</sub> O <sub>3.98</sub>		
88 K [11]	-23.7	-1.6
MnTi <sub>0.15</sub> Fe <sub>1.85</sub> O <sub>4</sub>		
4.2 K [13]	101	-230
Mn <sub>0.75</sub> Ni <sub>0.24</sub> Fe <sub>1.98</sub> O <sub>4</sub> [12]	-4.1	
90 K	-13.5	-10
Mn <sub>0.57</sub> Ni <sub>0.20</sub> Fe <sub>2.23</sub> O <sub>4</sub> [12]	-2.8	
90 K	-9.5	-8
Mn <sub>0.53</sub> Mg <sub>0.75</sub> Co <sub>0.023</sub> Fe <sub>1.71</sub> O <sub>3.98</sub> [14]	-2.8	
88 K	18.9	-147
Mn <sub>0.53</sub> Mg <sub>0.75</sub> Co <sub>0.076</sub> Fe <sub>1.71</sub> O <sub>4.04</sub> [14]	-0.7	
88 K	94	-423
Mn <sub>0.90</sub> Co <sub>0.009</sub> Fe <sub>1.09</sub> O <sub>4</sub> 82 K [15]	19.8	-104
Mn <sub>1.03</sub> Co <sub>0.019</sub> Fe <sub>1.94</sub> O <sub>4</sub> [16]	-22.2	
160 K	91.8	
NiFe <sub>2</sub> O <sub>4</sub> [17*]	-6.9	0.2
4.2 K	-8.9	-0.06
Ni <sub>0.76</sub> Fe <sub>2.16</sub> O <sub>4</sub> [18]	-3.9	
77 K	-4.2	
Ni <sub>0.20</sub> Fe <sub>2.80</sub> O <sub>4</sub> [12]	-6.7	
90 K	12.3	-9
Ni <sub>0.55</sub> Mn <sub>0.17</sub> Fe <sub>2.25</sub> O <sub>4</sub> [12]	-4.7	
90 K	-6.6	-9



TABLE 5f-19. MAGNETOCRYSTALLINE ANISOTROPY CONSTANTS OF SOME CUBIC OXIDES AND OTHER CUBIC MATERIALS [1] (Continued)

Material	$10^{-4}K_1$	$10^{-4}K_2$
Ni <sub>0.2</sub> Zn <sub>0.45</sub> Fe <sub>2.25</sub> O <sub>4</sub> [19].....	-1.7	
88 K.....	-16	
Ni <sub>0.7</sub> Co <sub>0.004</sub> Fe <sub>2.2</sub> O <sub>4</sub> [20].....	-1.0	
77 K.....	-19.6	
Fe <sub>3</sub> O <sub>4</sub> [21].....	-13.0	-4.4
150 K.....	-4.0	-4.2
Ga <sub>0.44</sub> Fe <sub>0.93</sub> <sup>2+</sup> Fe <sub>1.61</sub> <sup>3+</sup> O <sub>4</sub> [22].....	-80.9	
200 K.....	-122	
Ga <sub>0.76</sub> Fe <sub>0.94</sub> <sup>2+</sup> Fe <sub>1.25</sub> <sup>3+</sup> O <sub>4</sub> [22].....	-36.9	
200 K.....	-75.7	
Al <sub>0.21</sub> Fe <sub>0.99</sub> <sup>2+</sup> Fe <sub>1.81</sub> <sup>3+</sup> O <sub>4</sub> [23].....	-12	
120 K.....	-10	
Fe <sub>2.9</sub> Ti <sub>0.10</sub> O <sub>4</sub> [21].....	-25.0	4.8
80 K.....	2.3	-4.0
Fe <sub>2.69</sub> Ti <sub>0.31</sub> O <sub>4</sub> [21].....	-18.1	
80 K.....	-1.0	
Fe <sub>2.99</sub> Co <sub>0.01</sub> O <sub>4</sub> [24].....	0	
130 K.....	69.2	
CoFe <sub>2</sub> O <sub>4</sub> [25].....	260	
Co <sub>0.8</sub> Fe <sub>2.2</sub> O <sub>4</sub> [20].....	290	
77 K.....	440	
Co <sub>1.1</sub> Fe <sub>1.9</sub> O <sub>4</sub> [20].....	180	
Co <sub>0.7</sub> Zn <sub>0.3</sub> Fe <sub>2.0</sub> O <sub>4</sub> [26].....	23.6	
Co <sub>0.3</sub> Zn <sub>0.2</sub> Fe <sub>2.3</sub> O <sub>4</sub> [20]	150	
Li <sub>0.53</sub> Fe <sub>2.45</sub> O <sub>4</sub>		
Ordered.....	-8.3 [27]	-0.2 [28*]
77 K.....	-12.7 [27]	-9.7 [28*]
Disordered.....	-9.0 [27]	0.06 [28*]
77 K.....	-16.2 [27]	-3.2 [28*]
Mg <sub>0.94</sub> Fe <sub>0.06</sub> <sup>2+</sup> Fe <sub>2</sub> <sup>3+</sup> O <sub>4</sub>		
Low $M_s$ [29].....	-4.6	
77 K.....	12.8	
High $M_s$ .....	-4.2	
77 K.....	-15.3	
Mg <sub>0.75</sub> Fe <sub>0.25</sub> <sup>2+</sup> Fe <sub>2</sub> <sup>3+</sup> O <sub>4</sub> [30].....	-4.8	
88 K.....	-12.2	
Mg <sub>0.50</sub> Fe <sub>0.50</sub> <sup>2+</sup> Fe <sub>2</sub> <sup>3+</sup> O <sub>4</sub> [30].....	-5.8	
88 K.....	-6.0	
Mg <sub>0.8</sub> Fe <sub>2.2</sub> O <sub>4</sub> [11], 88 K.....	-10.9	-1.5
CuFe <sub>2</sub> O <sub>4</sub> [31].....	-0.04	
77 K.....	-2.06	
EuO [32] 1.5 K.....	$K_1/M = 190 \text{ Oe}^*$	
CdCr <sub>2</sub> Se <sub>4</sub> [33], 4.4 K.....	0.22-1.8*	
CdCr <sub>2</sub> S [33], 4.4 K.....	0.38-4.4*	

\* Values obtained from microwave measurements.

## References for Table 5f-19

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TABLE 5f-20. MAGNETOCRYSTALLINE ANISOTROPY CONSTANTS OF SOME NONCUBIC MATERIALS\*† (in ergs/cm<sup>3</sup>)

Material	10 <sup>-6</sup> K <sub>1</sub>	10 <sup>-6</sup> K <sub>2</sub>
Co [1] (Fig. 5f-33)	5.3	1.0
97 K	7.9	1.0
Gd [2]		
10 K	-0.85	2.5
Tb [3]		
205 K	$K_1 + \frac{8}{7}K_2 = -260$	
11 K	$K_1 + \frac{8}{7}K_2 = -830$	
Dy [3]		
152 K	$K_1 + \frac{8}{7}K_2 = -260$	
22 K	$K_1 + \frac{8}{7}K_2 = -750$	
1.8 wt. % Tb-Gd [4]		
190 K	-2.9	0.6
4.2 K	-13.1	6.6
1.3 wt. % Dy-Gd [4]		
180 K	-1.9	0.3
4.2 K	-8.8	4.2
MnBi [5]	$K_1 + K_2 = 12$	
88 K	$K_1 + K_2 = 0$	
Mn <sub>2</sub> Sb [6]	0.30	0.13
200 K	-0.50	0.03
Mn <sub>1.95</sub> Cr <sub>0.05</sub> Sb [6]	0.76	-0.12
200 K	0	
Mn <sub>3</sub> Ge <sub>3</sub> [7]	0.3	
77 K	4.2	
Fe <sub>3</sub> Ge <sub>3</sub> [8]	-5	
77 K	-8.5	
CrTe [9]		
283 K	-1.5	
0 K	-5.5	
CrO <sub>2</sub> [10‡]	$K_1/M = 450$ Oe	$K_2/M = 90$ Oe
4.2 K	$K_1/M = 690$ Oe	$K_2/M = 60$ Oe
Ga <sub>0.89</sub> Fe <sub>1.11</sub> O <sub>3</sub> [11], 4.2 K	(a-c plane) 3.22 (b-c plane) 5.65	
CrBr <sub>3</sub> [12‡], 1.5 K	0.94	
Fe <sub>7</sub> Se <sub>3</sub> [13]		
280 K	2.5	
4.2 K	35	
BaFe <sub>12</sub> O <sub>19</sub>	3.3 [14]	0 [15]
77 K	4.3 [14]	0 [15]
BaCo <sub>1.5</sub> Ti <sub>1.5</sub> Fe <sub>9</sub> O <sub>9</sub> [16]		
90 K	-1.05	
BaNi <sup>2+</sup> Ti <sup>4+</sup> Fe <sub>10</sub> O <sub>19</sub> [17]	0.7	
BaZn <sup>2+</sup> Ti <sup>4+</sup> Fe <sub>10</sub> O <sub>19</sub> [17]	1.4	
PbFe <sub>12</sub> O <sub>19</sub> [18]	2.2	0.030
2.3 K	2.8	0.062
Ba <sub>2</sub> Co <sub>2</sub> Fe <sub>12</sub> O <sub>22</sub> [17]	$K_1 + 2K_2 = -2.6$	
BaFe <sub>16</sub> O <sub>27</sub> [19]	3.41	0
77 K	4.31	0
BaCo <sub>0.5</sub> Fe <sub>1.5</sub> <sup>2+</sup> Fe <sub>16</sub> <sup>3+</sup> O <sub>27</sub> [19]	2.38	0.11
77 K	-0.04	2.14
BaCo <sub>1.5</sub> Fe <sub>0.5</sub> <sup>2+</sup> Fe <sub>16</sub> <sup>3+</sup> O <sub>27</sub> [19]	-0.66	0.63
77 K	-4.98	3.61
BaCo <sub>1.85</sub> Fe <sub>16.2</sub> O <sub>27</sub> [20]	$K_1 + \frac{8}{7}K_2 = -4.0$	
77 K	$K_1 + \frac{8}{7}K_2 = -7.3$	
BaCoZnFe <sub>14</sub> O <sub>27</sub> [16]		
77 K	-3.4	
Ba <sub>2</sub> Co <sub>2</sub> Fe <sub>24</sub> O <sub>41</sub> [14]	$K_1 + 2K_2 = -1.7$	
Ba <sub>2</sub> CoZnFe <sub>24</sub> O <sub>41</sub> [14]	$K_1 + 2K_2 = -0.8$	
77 K [16]	$K_1 + 2K_2 = -0.8$	

\* Unless otherwise specified, values are for room temperature.

† All materials are hexagonal except Ga<sub>0.89</sub>Fe<sub>1.11</sub>O<sub>3</sub> (orthorhombic), and Mn<sub>2</sub>Sb, Mn<sub>1.95</sub>Cr<sub>0.05</sub>Sb, CrO<sub>2</sub> (tetragonal).

‡ Obtained from microwave measurements.

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**5f-11. Magnetostriction.<sup>1</sup> Single Crystals.** When a cubic crystal is magnetized to saturation in a direction defined by the direction cosines  $\alpha_1, \alpha_2, \alpha_3$ , the fractional change in length measured in the direction  $\beta_1, \beta_2, \beta_3$  is given to the first approximation by

$$\left(\frac{\Delta l}{l}\right)_s = \lambda_s = \frac{3}{2}\lambda_{100}(\alpha_1^2\beta_1^2 + \alpha_2^2\beta_2^2 + \alpha_3^2\beta_3^2 - \frac{1}{3}) + 3\lambda_{111}(\alpha_1\alpha_2\beta_1\beta_2 + \alpha_2\alpha_3\beta_2\beta_3 + \alpha_3\alpha_1\beta_3\beta_1)$$

<sup>1</sup> Prepared by A. E. Clark, U.S. Naval Ordnance Laboratory.

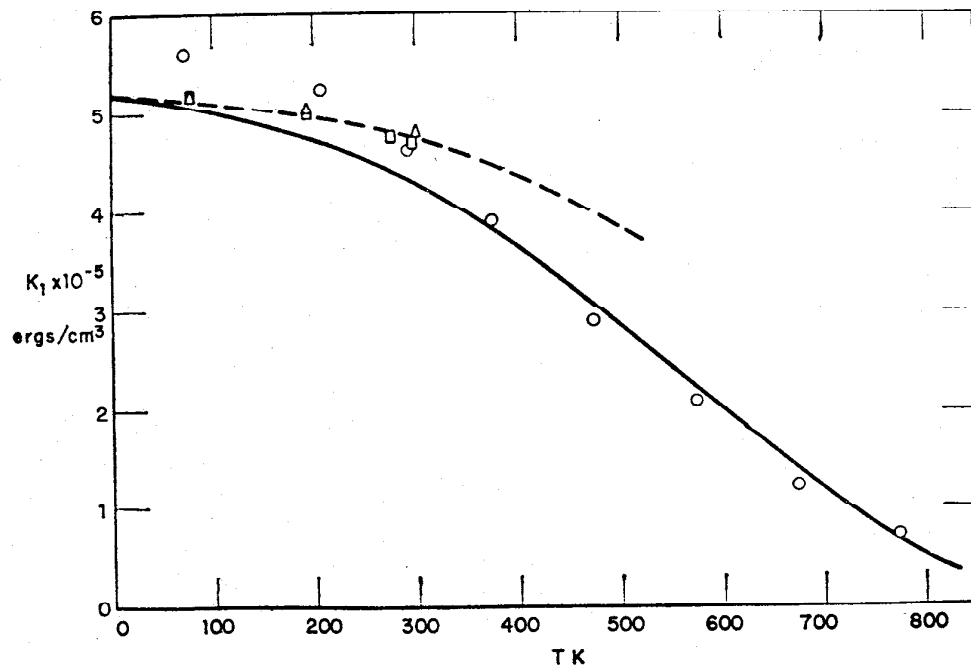


FIG. 5f-30. Measured values of  $K_1$  for iron plotted against temperature.  $\Delta$ —measurements of Graham.  $\square$ —measurements of Bozorth as given by Graham.  $\circ$ —older values of Bozorth as calculated from magnetization curves of Honda, Masumoto, and Kaya: ---  $5.2 \times 10^5 (\sigma/\sigma_0)^5$ . —  $5.2 \times 10^5 (\sigma/\sigma_0)^{10}$ .  $\sigma$  is the magnetization per unit mass. [From W. J. Carr, Jr., *J. Appl. Phys.* **31**, 69 (1960).]

provided that in the initial condition from which  $\lambda_s$  is measured, the domains are distributed equally among the easy directions of magnetization (six [100] directions in Fe, eight [111] directions in Ni). In any case, this equation gives the correct change in  $\lambda_s$  as the magnetization direction is varied. A five-constant expression which includes magnetization-direction cosines to the fourth power is sometimes used [1]. To lowest order there is no volume change associated with domain rotation. The constants  $\lambda_{100}$  and  $\lambda_{111}$  for some cubic materials are given in Tables 5f-21 and 5f-22 and in Fig. 5f-34.

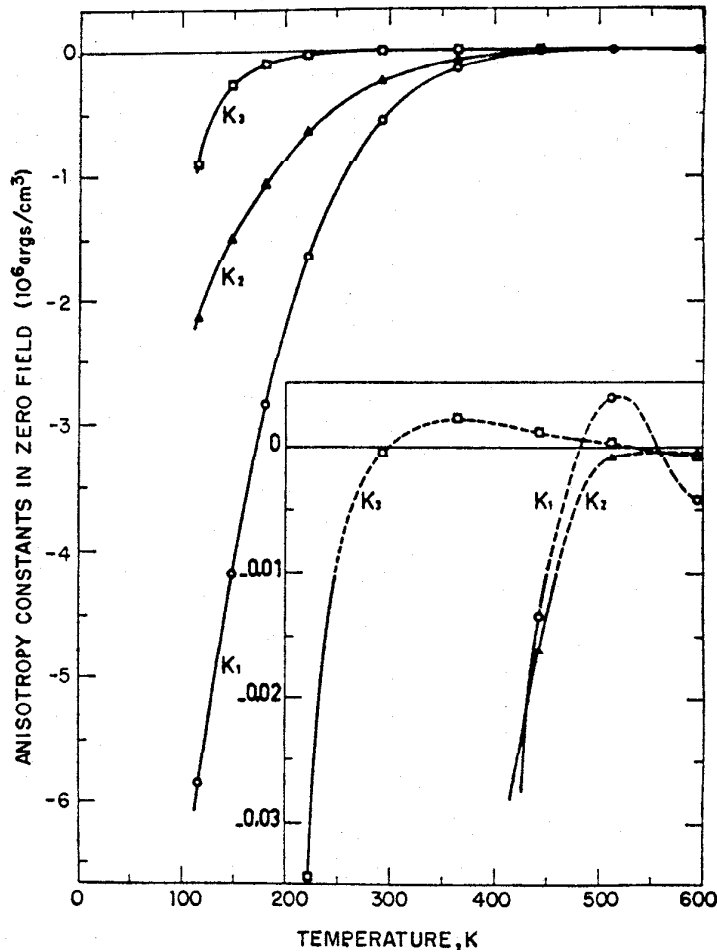


FIG. 5f-31. Temperature dependence of the anisotropy constants of nickel. [From G. Aubert, *J. Appl. Phys.* **39**, 504 (1968).]

The saturation magnetostriction of hexagonal crystals is described to lowest order by the following four-constant expression:

$$\lambda_s = \lambda_1^\alpha (\beta_1^2 + \beta_2^2) (\alpha_3^2 - \frac{1}{3}) + \lambda_2^\alpha \beta_3^2 (\alpha_3^2 - \frac{1}{3}) + \lambda^\gamma [\frac{1}{2} (\beta_1^2 - \beta_2^2) (\alpha_1^2 - \alpha_2^2) + 2\beta_1 \beta_2 \alpha_1 \alpha_2] + 2\lambda^\epsilon (\beta_1 \alpha_1 + \beta_2 \alpha_2) \beta_3 \alpha_3$$

In this equation  $\lambda^\gamma$  and  $\lambda^\epsilon$  represent distortions which lower the symmetry of the crystal (as do  $\lambda_{100}$  and  $\lambda_{111}$  in cubic crystals), while  $\lambda_1^\alpha$  and  $\lambda_2^\alpha$  represent linear changes respectively along a direction in the basal plane and along the  $c$  axis [2]. The direction cosines are referred to rectangular axes so chosen that the 3 axis lies along the hexagonal  $c$  axis. The 1 and 2 axes are any two perpendicular directions in the basal plane

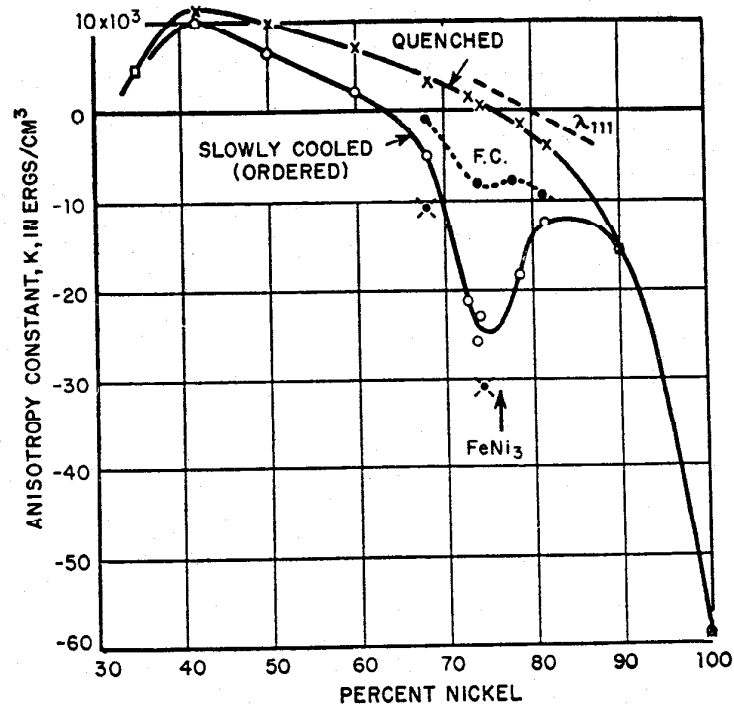


FIG. 5f-32. Magnetic anisotropy constants of quenched and of slowly cooled Fe-Ni alloys. Approximate rates of cooling,  $10^5$  and  $2.5^\circ\text{C/hr}$ , respectively, from  $600$  to  $300^\circ\text{C}$ . Broken line F.C. shows values for  $55^\circ\text{C/hr}$ . Line  $\lambda_{111}$  shows composition at which magnetostriction in [111] direction goes through zero. Single low points at 68 and 74 percent nickel are for cooling rate of about  $1.5^\circ\text{C/hr}$ . [From R. M. Bozorth and J. G. Walker, *Phys. Rev.* **89**, 624 (1953).]

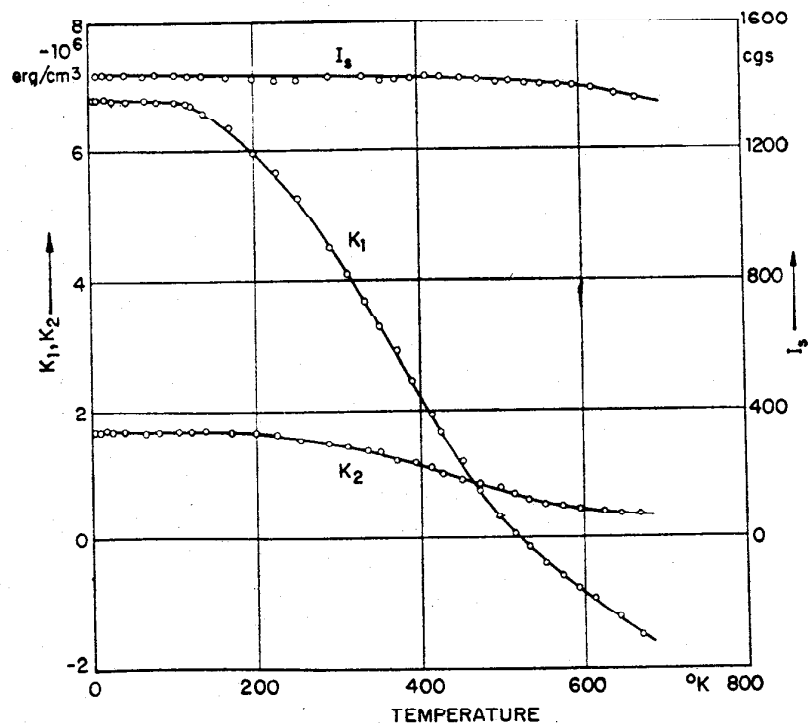


FIG. 5f-33. Temperature dependence of the spontaneous magnetization  $M_s$  and the anisotropy constants  $K_1$  and  $K_2$  for hexagonal cobalt. [From R. Pauthenet, Y. Barnier, and G. Rimet, *J. Phys. Soc. Japan* **17**, suppl. B1, 309 (1962).]

The magnetostriction constants of some hexagonal crystals are given in Table 5f-23. The volume change associated with magnetization rotation from the basal plane to the hexagonal axis is  $2\lambda_1^\alpha + \lambda_2^\alpha$ . In cobalt [3], the volume change is  $26 \times 10^{-6}$ .

Many coefficients are required to describe the magnetostriction of crystals of lower symmetry [4].

*Polycrystalline Materials.* If a polycrystal has randomly oriented crystallites and equally distributed domains, its fractional change in length upon application of a saturating magnetic field is given by

$$\lambda = \frac{3}{2} \bar{\lambda}_s (\cos^2\theta - \frac{1}{3})$$

$\theta$  is the angle between the direction of the magnetization and the direction in which the change is measured. In a cubic material the saturation magnetostriction  $\bar{\lambda}_s$  can be calculated from

$$\bar{\lambda}_s = (\frac{2}{3} - K)\lambda_{100} + (\frac{3}{5} + K)\lambda_{111}$$

Here  $K = \frac{1}{8} \log [2C_{44}/(C_{11} - C_{12})]$  where  $C_{11}$ ,  $C_{12}$ , and  $C_{44}$  are the elastic moduli [5]. For an elastically isotropic material,  $K = 0$ .

Values of  $\bar{\lambda}_s$  at room temperature for some alloys and compounds are given in Table 5f-24. (The specimens do not necessarily have randomly oriented crystallites.) The fractional change in length parallel to an applied magnetic field of a few hard magnetic materials is illustrated in Fig. 5f-35. The approach to saturation of the longitudinal magnetostriction of iron, cobalt, and nickel are shown in Fig. 5f-36.

*Forced Magnetostriction.* Above technical saturation, where domain effects are no longer important, the dimensions of a magnetic body continue to change with increasing magnetic field. In many materials, the distortion is essentially an isotropic volume change and is frequently referred to as the high-field "volume" magnetostriction  $\omega$ . Unlike the shape magnetostriction which arises primarily from the strain dependence of the anisotropy energy, the isotropic volume magnetostriction results from the dependence of the exchange on strain. It is maximum near the Curie temperature and is linear with field at temperatures appreciably below. Room-temperature values of  $\delta\omega/\delta H$  for some materials are listed in Table 5f-25. Although the anisotropic part of the forced magnetostriction is small in cubic crystals, it may be large in single crystals of lower symmetry. In Gd, for example, at 300 K the forced magnetostriction parallel to the hexagonal  $c$  axis is  $+280 \times 10^{-10}/\text{Oe}$  whereas it is  $-13 \times 10^{-10}/\text{Oe}$  for the magnetostriction parallel to the  $a$  axis [6].

In ferrites the forced magnetostriction changes sign at the magnetization compensation temperatures. Such reversals have been observed in the ferrimagnetic rare-earth iron garnets [7].

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TABLE 5f-21. MAGNETOSTRICTION CONSTANTS OF SOME CUBIC METALS

Metal	$\lambda_{100} \times 10^6$			$\lambda_{111} \times 10^6$			Reference
	4 K	77 K	~293 K	4 K	77 K	~293 K	
Fe.....	.....	.....	20	.....	.....	-21	1
	23	23	24	-30	-30	-22	2
Ni.....	.....	.....	-51	.....	.....	-23	3
	.....	-57	-54	.....	-28	-23	4
Fe + 3.9 wt. % Si.....	16	16	25	-2	-2	-3	2
Fe + 5.6 wt. % Si.....	-8	-7	7	2	2	2	2
Fe + 4.6 wt. % Al.....	32	34	40	-20	-19	-14	2
Fe + 8.6 wt. % Al.....	.....	85	92	.....	-8	-6	2
Fe + 5.32 wt. % Ge.....	.....	22	26	.....	-20	-14	2
Fe + 6.07 wt. % V.....	.....	.....	28	.....	.....	-12	5
Fe + 14.4 wt. % V.....	.....	.....	43	.....	.....	-10	5
Fe + 5.72 wt. % Mo.....	.....	.....	33	.....	.....	-10	5
Fe + 7.24 wt. % Mo.....	.....	.....	39	.....	.....	-8	5
Fe + 14.7 wt. % Cr.....	.....	.....	51	.....	.....	-6	5
Fe + 10.0 wt. % Cr.....	.....	.....	52	.....	.....	-3	5
Fe + 1.39 wt. % Ti.....	.....	.....	18	.....	.....	-16	5
Fe + 2.09 wt. % Ti.....	.....	.....	15	.....	.....	-13	5
Fe + 2.47 wt. % Sn.....	.....	.....	13	.....	.....	-15	5
Fe + 3.70 wt. % Sn.....	.....	.....	12	.....	.....	-14	5

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TABLE 5f-22. ROOM-TEMPERATURE MAGNETOSTRICTION OF SOME MAGNETIC COMPOUNDS

Compound	$\lambda_{100} \times 10^6$	$\lambda_{111} \times 10^6$	Ref.	Compound	$\lambda_{100} \times 10^6$	$\lambda_{111} \times 10^6$	Ref.
Fe <sub>3</sub> O <sub>4</sub> .....	-20	80	1	Er <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub> ....	1	-5	5, 6
Co <sub>0.8</sub> Fe <sub>2.2</sub> O <sub>4</sub> ..	-590	120	2	Eu <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub> ....	21	2	6
NiFe <sub>2</sub> O <sub>4</sub> .....	-46	-22	3	Gd <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub> ....	0	-3	6
Ni <sub>0.8</sub> Fe <sub>2.2</sub> O <sub>4</sub> ..	-36	-4	2	Tb <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub> ....	-3	12	6
MnFe <sub>2</sub> O <sub>4</sub> .....	-35	-1	2	Tm <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub> ....	1	-5	6
Y <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub> ....	-1	-3	4, 6	Yb <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub> ....	1	-5	6
Dy <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub> ....	-14	-8	5, 6	CoO (10 kOe, 77 K).....	9	..	7
Ho <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub> ....	-6	-4	5, 6				

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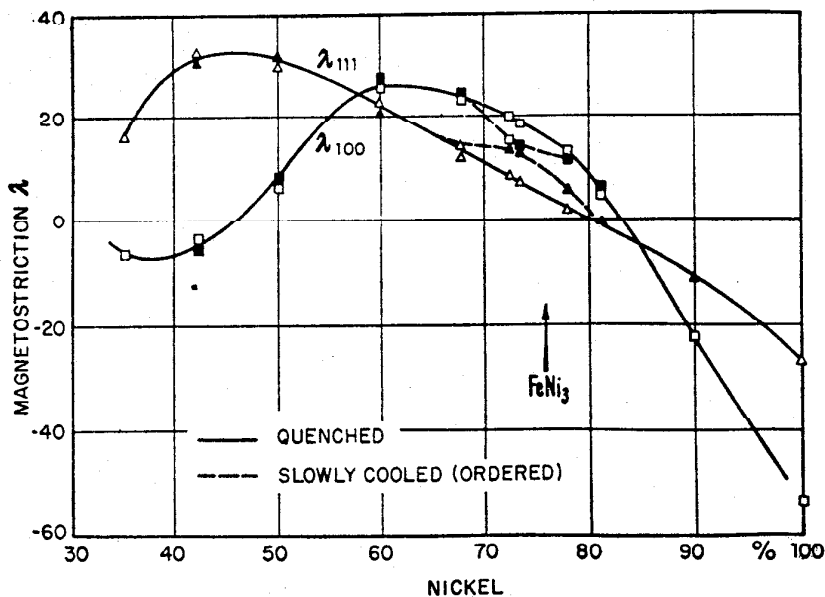
TABLE 5f-23. MAGNETOSTRICTION OF SOME HEXAGONAL CRYSTALS

Crystal	T, K	$\lambda^\gamma \times 10^6$	$\lambda^\epsilon \times 10^6$	$\lambda_1^\alpha \times 10^6$	$\lambda_2^\alpha \times 10^6$	Ref.
Co.....	RT	50	-233	70	-110	1
MnBi.....	RT	-45*	.....	37*	-50*	2
Gd.....	0	105	34	143	-105	3,4
Gd.....	200	14	4	42	-110	3,4
Tb.....	0	8,500	15,000†	-2,600†	9,000†	5,6
Tb.....	150	4,700*	.....	.....	.....	5
Dy.....	0	9,000	5,500†	.....	.....	7,8
Dy.....	200	24*	10*	.....	.....	7,8
Ho.....	0	2,300	.....	.....	.....	9
Ho.....	150	3*	.....	.....	.....	9
Er.....	0	-5,100†	.....	.....	.....	10
Er.....	150	-1*	.....	.....	.....	10

\*  $H = 10$  kOe    † Extrapolated from paramagnetic region.

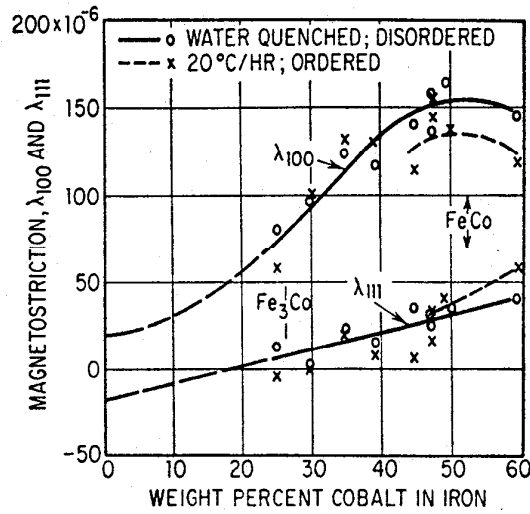
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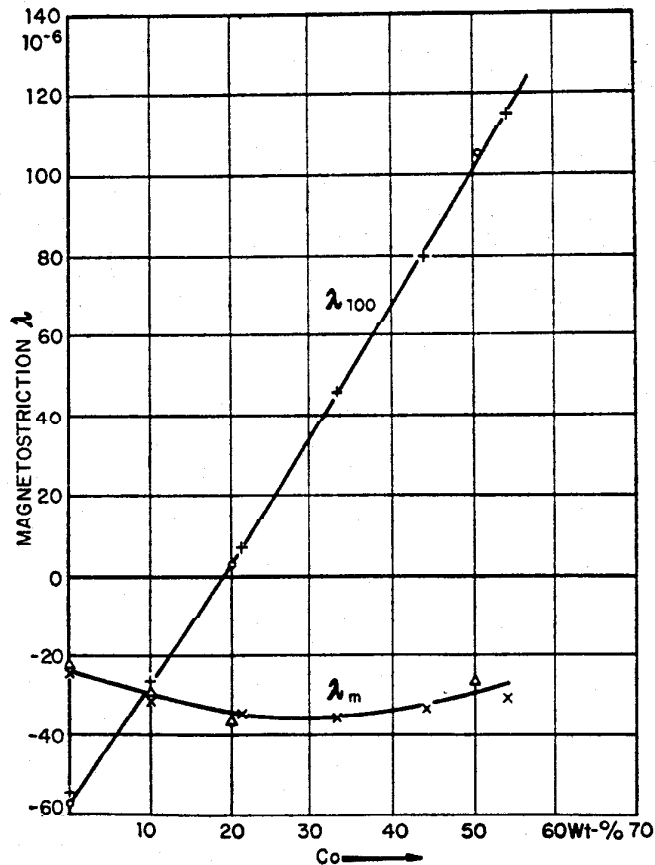


(a)

FIG. 5f-34a. See legend on page 5-212.



(b)



(c)

FIG. 5f-34. Saturation magnetostriction constants of iron-nickel, iron-cobalt, and nickel-cobalt alloys. (a) Iron-nickel, from R. M. Bozorth and J. G. Walker: *Phys. Rev.* **89**, 624 (1953). (b) Iron-cobalt from R. C. Hall: *J. Appl. Phys. Suppl.* **31**, 157S (1960). (c) Nickel-cobalt; +, × taken from M. Yamamoto and T. Nakamichi: *J. Phys. Soc. (Japan)* **13**, 228 (1958); O, Δ from R. C. Hall: *J. Appl. Phys.* **30**, 816 (1959). (Figure taken from "Secondary Effects in Ferromagnetism," W. J. Carr, "Handbuch der Physik," Vol. XVIII, 12 Springer-Verlag, OHG, Berlin, 1966.

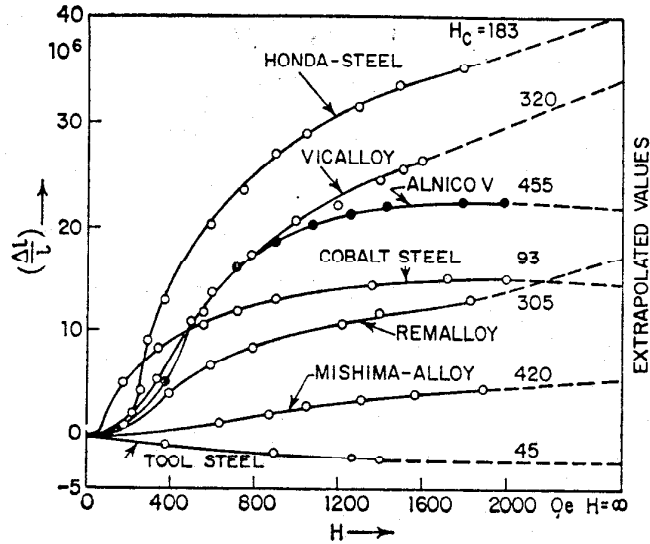


Fig. 5f-35. The longitudinal change in length of a few hard magnetic materials as a function of magnetic field.  $H_c$  is the coercive force. [From E. A. Nesbitt, *J. Appl. Phys.* **21**, 879 (1950).]

TABLE 5f-24. SATURATION MAGNETOSTRICTION OF SOME POLYCRYSTALLINE MATERIALS

Material, wt. %	$\lambda_s \times 10^6$	Ref.	Material, wt. %	$\lambda_s \times 10^6$	Ref.
Fe.....	-9	1	20% Co, 80% Ni.....	-21	2, 3
Co.....	-62*	2	Gd.....	-7†	6
Ni.....	-33	3	Fe <sub>3</sub> O <sub>4</sub> .....	40	7
80% Fe, 20% Co.....	32*	4	MnFe <sub>2</sub> O <sub>4</sub> .....	-5	7
70% Fe, 30% Co.....	35*	4	CoFe <sub>2</sub> O <sub>4</sub> .....	-110	7
40% Fe, 60% Co.....	68*	4	MgFe <sub>2</sub> O <sub>4</sub> .....	-6	7
30% Fe, 70% Co.....	57*	4	Li <sub>0.5</sub> Fe <sub>2.5</sub> O <sub>4</sub> .....	-8	7
20% Fe, 80% Co.....	32*	4	NiFe <sub>2</sub> O <sub>4</sub> .....	-20	7
80% Fe, 20% Ni.....	30†	5	CuFe <sub>2</sub> O <sub>4</sub> .....	-10	8
70% Fe, 30% Ni.....	10†	5	Y <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub> .....	-2	9
40% Fe, 60% Ni.....	25†	5	Gd <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub> .....	~ -1	10
20% Fe, 80% Ni.....	2†	5	Tb <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub> .....	+240§	11
10% Fe, 90% Ni.....	-15†	5	Dy <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub> .....	-100§	11
60% Co, 40% Ni.....	6*, 31	2, 3	Er <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub> .....	-2§	11
50% Co, 50% Ni.....	~0*, 19	2, 3			

\*  $H = 900$  Oe    †  $H = 1,050$  Oe    ‡  $T = 200$  K    §  $T = 100$  K,  $H = 5$  kOe

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TABLE 5f-25. HIGH FIELD VOLUME MAGNETOSTRICTION

Material, wt. %	$\delta\omega \times 10^{10}/\delta H, \text{Oe}^{-1}$	Ref.	Material, wt. %	$\delta\omega \times 10^{10}/\delta H, \text{Oe}^{-1}$	Ref.
Fe.....	6	1	40 % Ni, 60 % Fe	~60	4
Co.....	~6	2	3 % Al, 97 % Fe.	8	5
Ni.....	-0.6	3	15 % Al, 85 % Fe	14	5
20 % Ni, 80 % Fe	~15	4	Fe <sub>3</sub> O <sub>4</sub> .....	-0.7	6
30 % Ni, 70 % Fe	~200	4	Gd.....	150	7

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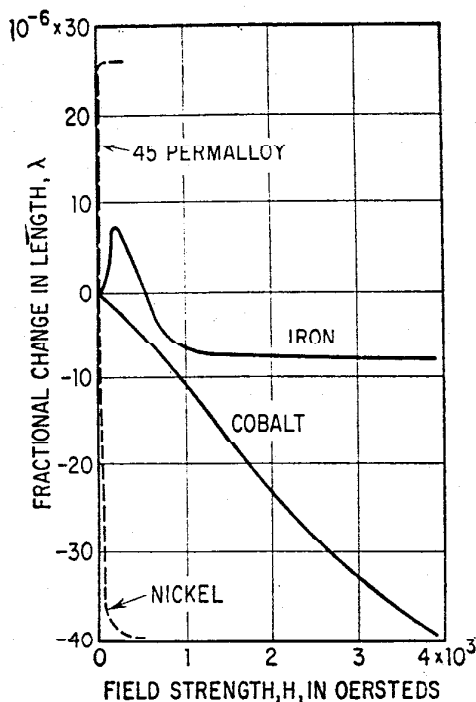


FIG. 5f-36. Longitudinal magnetostriction of iron, cobalt, nickel, and 45-permalloy as a function of field. (Figure taken from R. M. Bozorth, "Ferromagnetism," D. Van Nostrand Company, Inc., Princeton, N.J., 1951.)

**5f-12. Hall Constants of Ferromagnetic Elements and Alloys.<sup>1</sup>** In ferromagnetic materials the Hall effect (see Sec 5a for definition) has its origin in two independent, experimentally distinguishable mechanisms. One is the result of the usual Lorentz force and is proportional to  $B$ , the magnetic induction in the material, while the second arises from spin-orbit coupling and is proportional to  $M$ , the macroscopic magnetiza-

<sup>1</sup> Compiled by A. C. Ehrlich and A. I. Schindler, U.S. Naval Research Laboratory.

tion. A conventional description of the Hall effect is given in terms of the Hall resistivity  $\rho_H$  by the following expression

$$\rho_H = R_0 B + R_s M$$

where  $\rho_H$  is the Hall electric field per unit current density,  $R_0$  is the ordinary Hall coefficient, and  $R_s$  (sometimes designated by  $R_1$ ) is the spontaneous (or extraordinary) Hall coefficient. Tables 5f-26 through 5f-30 list values of  $R_0$  and  $R_s$  in cubic meters per coulomb ( $1 \text{ m}^3/\text{coul} = 10^{-2} \text{ ohm-cm/Oe}$ ) at various temperatures. By convention, a negative (positive) sign for  $R_0$  indicates electron (hole) type conduction.

TABLE 5f-26. HALL CONSTANTS OF POLYCRYSTALLINE ELEMENTS  
( $1 \text{ m}^3/\text{coul} = 10^{-2} \text{ ohm-cm/Oe}$ )

Element	T, K	$R_0 \times 10^{11}$ , $\text{m}^3/\text{coul}$	$R_s \times 10^{11}$ , $\text{m}^3/\text{coul}$	Ref.*	Element	T, K	$R_0 \times 10^{11}$ , $\text{m}^3/\text{coul}$	$R_s \times 10^{11}$ , $\text{m}^3/\text{coul}$	Ref.*
Fe.....	301	2.28	66.8	1†	Ni	296	-5.67	-49.2	3
	231	2.67	26.6			273	-5.55	-38.9	
	169	2.15	3.77			194	-5.00	-12.6	
	112	1.58	1.02			117	4.10	2.82	
	77	0.56	-0.08			96	-3.82	-1.96	
Co.....	293	-12.4	8.4	2‡	77	-3.53	-1.70	4§	
	273	-13.6	7.2		4.15	-7.00	-0.6		
	193	-11.8	-0.9						
	77	-13.2	-4.2						

\* After Table 5f-30.

† For higher-temperature data see Volkenshtein et al. [23].

‡ Contains additional data concerning dependence of  $R_0$  and  $R_s$  on metallurgical treatment.

§ These data were obtained on a polycrystal in the "high field limit" ( $\omega_c \tau \gg 1$ ).

In Tables 5f-26 through 5f-30 certain classes of data have been expressly omitted. These are (1) low-temperature (i.e., where the residual resistivity dominates the thermal resistivity) measurements on "pure" metals in the "low field limit," i.e., when  $\omega_c \tau < 1$ ,  $\omega_c$  being the cyclotron frequency, and  $\tau$  the relaxation time; and (2) single-crystal measurements made primarily as studies of Fermi surface topology. Limited single-crystal studies have been made on both the 3d and the rare-earth 4f ferromagnetic metals. Both Hall coefficients for Fe are isotropic and are similar to polycrystalline data above 70 K. Some single-crystal rare-earth data and references to single-crystal work in other materials are given at the end of this compilation.

TABLE 5f-27. HALL CONSTANTS OF BINARY ALLOYS WITH NICKEL

Alloy, atomic %	Ref.*	T, K	$R_0 \times 10^{11}$ , m <sup>3</sup> /coul	$R_s \times 10^{11}$ , m <sup>3</sup> /coul	Alloy, atomic %	Ref.*	T, K	$R_0 \times 10^{11}$ , m <sup>3</sup> /coul	$R_s \times 10^{11}$ , m <sup>3</sup> /coul		
Fe 0.07...	3††	292	-5.74	-50.8	Cu 1.30...	3††	293	-6.43	-75.0		
		77	-3.66	-2.05			194	-6.14	-29.8		
		4.15	-3.07	-1.72			77	-6.63	-9.0		
Fe 1.08...	3††	293	-0.83	-09.8	Cu 10.....	8†	4.15	-5.99	-19.3		
		77	-3.85	-5.60			293	-10.8	-225		
		4.15	-0.83	-6.80			77	-14.4	-83.5		
Fe 5.20...	3††	292	-10.3	-78.9	Cu 20.....	8†	301	-14.5	-512		
		77	-7.70	-9.04			77	-19.8	-194		
		4.15	-6.49	-10.3			293	-13	-783		
Fe 10.5...	5	290	-17	-20	Cu 30.....	8§†	77	-19.5	-465		
		77	-4.5	-12			14	-21.2	-414		
		290	-17	10.4			77	-14.8	152		
Fe 16.....	5	77	-22	6.6	Cu 50.....	8§†	20	-10.0	46.4		
		20	-23.5	4.6			303	-6.50	-73.3		
		293	-20.6	34.0			77	-5.01	-8.40		
Fe 20.9...	6†	293	-21.1	67.5	Pd 2.....	9††	4	-3.80	-11.07		
Fe 25.3...	6†	293	-21.3	63.5			Pd 5.....	9††	306	-6.68	-104
Fe 33.7...	0†	293	-21.3	63.5					77	-6.53	-13.0
Fe 80.....	1†	313	-15.2	423	4	-5.83			-13.0		
Fe 85.....	1†	309	-10.9	454	Pd 10.....	9†	301	-7.37	-132		
		77	-11.0	195			77	-7.12	-23.6		
		77	-2.59	395			4	-6.81	-19.8		
Fe 90.....	1†	303	-2.55	159	Pd 30.....	9††	301	-9.69	-349		
		77	2.55	279			77	-10.0	-93.8		
		299	-0.90	279			4	-10.4	-75.7		
Fe 95.....	1†	77	5.72	84.3	Pd 60.....	9††	300	-11.0	-801		
		77	3.15	85.0			77	-12.8	-300		
		77	0.24	2.49			4	-13.1	-242		
Co 0.51...	3††	293	-5.86	-58.4	Al 8.....	5	293	-10	-850		
		77	-3.17	-3.89			77	-18	-410		
		4.15	-0.75	-1.50			20	-18	-360		
Co 10.....	5	290	-22.5	-73.8	Si 3.....	5	293	-11	-390		
		77	-11	0.3			77	-10	-190		
		20	-12	-4.8			20	-7	-180		
Co 11.....	7††	298	-11.3	-85.0	Sn 3.....	5	293	-20	-340		
Co 20.....	5	290	-19	-6.5			77	-9	-180		
77	-20	-1.5	20	-2.7			20	-8.5	-180		
Co 30.....	5	295	-13	19	V 7.....	10	293	-48	-2,200		
		77	-28	5.4			77	10.5	-2,550		
		20	-29	-3.2			20	-16	-2,370		
Co 53.....	7††	294	-19.6	52.3	Mo 3.....	10	293	-15	-1,070		
Co 85.....	7††	294	-16.4	30.6			77	-10.5	-824		
Co 98.0...	2††	293	-13.3	9.6			20	-11.5	-824		
Co 99.77..	2††	77	-15.5	-6.1	W 1.6.....	10	293	-11	-395		
		4.15	-15.9	-8.1			77	-10.5	-205		
		293	-13.7	9.2			20	-7	-203		
Cu 0.06...	3††	193	-12.9	-0.3	Mn 25....	11  ††	302	-12.6	298		
		77	-14.0	-4.4			20	-24.0	112		
		4.15	-15.0	-7.6			231	-13	1,100		
Cu 0.06...	3††	293	-5.70	-50.35	Mn 25....	11††#	20	-17	110		
		77	-3.52	-2.68							
		4.15	-3.40	-1.40							

\* After Table 5f-30.

† This reference contains data for alloys with compositions intermediate to those given here.

‡ This reference contains data for this alloy for temperature(s) additional to those given here.

§ Values for  $R_0$  are obtained from the slope  $\partial R_H / \partial B$  at high fields. In these alloys  $R_s(\partial M / \partial B)$  is great enough to cause errors in  $R_0$  as large as 15% since values of  $\partial M / \partial B$  are not well known.

|| Ordered.

# Disordered.

†† See also Volkenshtein et al. [25].

TABLE 5f-28. HALL CONSTANTS OF TERNARY AND QUATERNARY ALLOYS WITH NICKEL

Alloy, atomic %	Ref.*	T, K	$R_0 \times 10^{11}$ , m <sup>3</sup> /coul	$R_s \times 10^{11}$ , m <sup>3</sup> /coul
Cu 2, Fe 1.....	12	300	-7.53	-120
		77	-8.53	-16.7
Cu 4.5, Fe 2.5.....	12	20	-9.78	-11.9
		300	-10.5	-150
		77	-14.0	-38.9
Cu 10.7, Fe 20.2.....	13†	20	-15.3	-27.8
		300	-21.1	68.1
		169	-24.0	32.2
Cu 14.1, Fe 16.5.....	13†	77	-28.2	20.2
		20	-30.5	16.6
		305	-20.1	78.7
Cu 19.8, Fe 10.0.....	13†	77	-26.4	29.3
		20	-28.2	25.6
		305	-18.8	64.0
Cu 25.6, Fe 3.3.....	13†	77	-26.1	28.9
		20	-28.2	25.9
		305	-15.1	-287
Fe 15, Mo 5, Mn 0.5. Fe 16, Cu 5, Cr 2..... Mn4, Si 1.....	14†	77	-22.5	-163
		20	-24.7	-144
		300	-20	105
	14†	300	-20	289
	14†	300	—	337

\* After Table 5f-30.  
† This reference contains data for this alloy at temperature(s) additional to those given here and at intermediate compositions.

TABLE 5f-29. HALL CONSTANTS OF BINARY ALLOYS WITH IRON

Alloy, atomic %	Ref.*	T, K	$R_0 \times 10^{11}$ , m <sup>3</sup> /coul	$R_s \times 10^{11}$ , m <sup>3</sup> /coul
Co 0.5.....	15†	297	-2.66	146
		77	-3.43	27.3
Co 15.....	15†	299	-12.30	251
		77	-12.91	136
Co 35.....	15†	300	-21.03	33.9
		77	-24.89	16.1
Co 60.....	15†	300	-8.87	10.4
		77	-8.29	4.91
Co 75.....	15†	300	-9.94	15.2
		77	-9.69	4.92
Co 85.....	15†	298	-15.90	40.2
		77	-17.59	6.54
Cr 2.3.....	16†	315	5.1	220
		77	22	18
Cr 5.1.....	16†	4.2	18	79
		305	7.8	370
		77	24	42
Cr 12.7.....	16†	4.2	22	120
		308	5.7	640
		77	25	82
Cr 25.1.....	16†	4.2	41	79
		307	6.1	730
		77	15	98
Al 25.....	17†	4.2	25	51
		295	0.0	4,700
Si 1.30.....	18§†	300	—	496
		77	—	235
Si 5.09.....	18§†	300	—	1,910
		77	—	1,600

\* After Table 5f-30.

† This reference contains data for this alloy at temperature(s) additional to those given here and at intermediate compositions.

‡ Ordered.

§ See also Okamoto et al. [24].

TABLE 5f-30. HALL CONSTANTS OF SINGLE CRYSTALS

Element	Ref.	T, K	B in basal plane		B along c axis*	
			$R_0 \times 10^{11}$ , m <sup>3</sup> /coul	$R_s \times 10^{11}$ , m <sup>3</sup> /coul	$R_0 \times 10^{11}$ , m <sup>3</sup> /coul	$R_s \times 10^{11}$ , m <sup>3</sup> /coul
Gd.....	19†‡	240	52.3	-872	-27.2	-4,080
		200	8.7	-367	-9.4	-3,200
		150	-30.1	-161	8.5	-1,900
		100	-40.0	-167	25.0	-890
		50	-34.7	-29	38.9	-170
Dy.....	20	148	—	117		
		119	—	210		
		78	—	130		
		39	—	22		
Tb.....	21	162	29.8	163		
		119	-8.5	200		
		79	-11.7	82.2		
		40	-15.8	5.7		
Fe.....	22	4 to 300	-10 to 1	-1 to 50		
Co.....	2, 23	4 to 300	10	-10 to 10		
Ni.....	23	4 to 300	5	50		

\* Applies only to rare-earth elements.

† See also Volkenshtein [26].

‡ This reference contains data for this alloy for temperature(s) additional to those given here.

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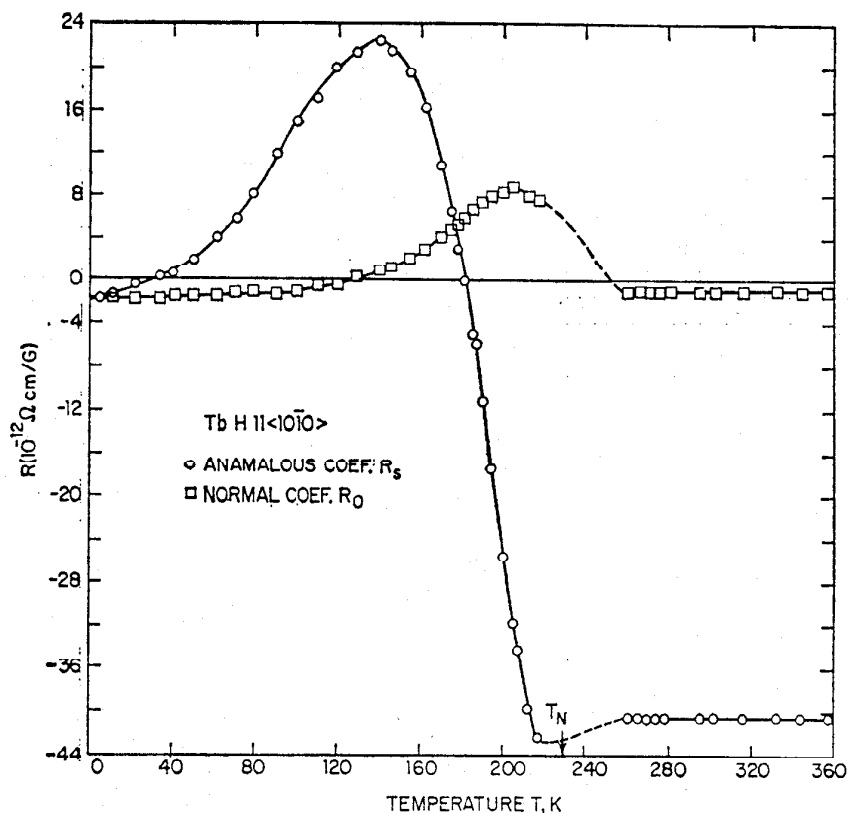


Fig. 5f-37. Temperature dependence of the anomalous and normal Hall coefficients for a single crystal of the heavy rare-earth element terbium. The sign change in  $R_s$  and the unique maximum occurring near  $0.6T_N$  were found also in Dy but were not observed in the S-state ion Gd or in the iron-group elements. The different temperature dependence in Gd is attributed to the absence of orbital angular momentum of the 4f ion. The constant value of  $R_s$  in the paramagnetic region is a consequence of the dominance of spin-disorder scattering. The broad rise in  $R_0$  below  $T_N$ , which remains after correction for the high field susceptibility, indicates a field dependence of the scattering. This effect is characteristic of Gd also. [After J. J. Rhyne, *J. Appl. Phys.* **40**, 1001 (1969)—recent data included by the editors; see also *Phys. Rev.* **172**, 523 (1968), and R. S. Lee and S. Legvold; *Phys. Rev.* **162**, 431 (1967).]

**5f-13. Faraday Effect. Magneto-optical Rotation.**<sup>1</sup> Linearly polarized light incident upon a magnetic material in which the magnetization is parallel to the light path emerges as elliptically polarized light. The major axis of the emergent elliptical light is rotated by the magnetization through an angle  $\theta$  relative to the vibration direction of the incident light.  $\theta$  is the Faraday rotation and is proportional to the magnetization  $\mathbf{M}$  of the material and also to the path length  $L$  in the material,

$$\theta = KLM$$

where the constant of proportionality  $K$  is known as *Kundt's constant* with the units deg/gauss-cm. The sign of the rotation is positive if the major axis of the ellipse is rotated in the same direction as the current flow in a solenoid used to create the magnetization  $\mathbf{M}$ . Table 5f-31A gives values of saturation rotation

$$\frac{\theta_s}{L} = KM_s$$

( $\mathbf{M}_s$  is the saturation magnetization) for some ferromagnetic or ferrimagnetic materials below their Curie temperature.

<sup>1</sup> Prepared by James C. Suits, IBM Research Center, San Jose, Calif.

TABLE 5f-31. MAGNETO-OPTICAL ROTATION OF VARIOUS MATERIALS

## A. Faraday Rotation: Ferromagnetic and Ferrimagnetic

Material	T, K	Saturation rotation, deg/cm	Wavelength, nm	Ref.
Fe.....	RT	347,000	546	1
Co.....	RT	363,000	546	1
Ni.....	RT	98,000	546	1
Gd.....	93	-325,000	589	2
EuO.....	5	85,000	800	3
EuSe.....	4.2	140,000	750	4
CrCl <sub>3</sub> .....	1.5	3,000	385	5
CrBr <sub>3</sub> .....	1.5	500,000	470	5
CrI <sub>3</sub> .....	1.5	150,000	950	5
CdCr <sub>2</sub> Se <sub>4</sub> .....	82	-9,200	1170	6
CrO <sub>2</sub> .....	RT	135,000	1000	7
MnBi.....	RT	570,000	750	8
RbNi <sub>10.75</sub> Co <sub>0.25</sub> F <sub>3</sub> .....	77	500	550	9
RbFeF <sub>3</sub> .....	82	3,300	300	10
FeRh.....	348	90,500	700	7
MgFe <sub>2</sub> O <sub>4</sub> .....	RT	-700	1100	11
Li <sub>0.5</sub> Fe <sub>2.5</sub> O <sub>4</sub> .....	RT	-970	1100	11
NiFe <sub>2</sub> O <sub>4</sub> .....	RT	27,000	330	12
CoFe <sub>2</sub> O <sub>4</sub> .....	RT	44,000	360	12
YFeO <sub>3</sub> .....	RT	8000	600	13
BaFe <sub>12</sub> O <sub>19</sub> .....	RT	160	6000	11
Ba <sub>2</sub> Zn <sub>2</sub> Fe <sub>12</sub> O <sub>22</sub> .....	RT	80	8000	11
Y <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub> .....	RT	4,000	530	14
Gd <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub> .....	RT	95,000	330	15
Ho <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub> .....	RT	60	1100	16
Er <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub> .....	RT	65	3500	17
Eu <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub> .....	RT	-760	3100	18
FeBO <sub>3</sub> .....	RT	4,800	480	19

## B. Faraday Rotation: Paramagnetic and Diamagnetic

Material	Room-temperature Verdet constant V, min/Oe-cm	Wavelength, nm	Ref.
EuO.....	-10.0	1200	20
EuF <sub>2</sub> .....	-6.6	435	20
TbAlG.....	-2.256	405	21
Eu glass.....	-2.55	450	22
Tb-Pr borate glass.....	-0.940	405	23
Corning 8363 (lead) glass..	0.10	600	24
Schott SFS-6 glass.....	0.490	366	25
AO soda-lime glass.....	0.074	334	25
Quartz.....	0.01664	546	26
NaCl.....	0.0410	546	27
CaF <sub>2</sub> .....	0.00883	589	28

For paramagnetic or diamagnetic materials or for ferromagnetic materials above their Curie temperature, the Faraday rotation is still proportional to  $\mathbf{M}$  but is usually described in terms of the applied field  $\mathbf{H}$ ,

$$\theta = VLH,$$

where the constant of proportionality  $V$  is known as the *Verdet constant* with the units  $\text{min}/\text{Oe-cm}$ . Table 5f-31B gives values of Verdet constant at room temperature for a few representative materials.

#### References for Tables 5f-31A and 5f-31B

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*Faraday Rotation at Microwave Frequencies.*<sup>1</sup> The Faraday effect which occurs at microwave frequencies is described by the relation

$$\theta = \frac{\omega}{2c} \sqrt{\epsilon} (\sqrt{\mu + \kappa} - \sqrt{\mu - \kappa}) L$$

where  $\theta$  = rotation, rad

$\omega$  = angular frequency, rad/sec

$c$  = velocity of light

$L$  = path length, cm

$\epsilon$  = dielectric constant

and  $\mu$  and  $\kappa$  are components of a permeability tensor which describes the behavior of materials under the combined influence of a static and an orthogonal r-f magnetic field. When  $\omega \gg 4\pi M\gamma$  and  $\omega \gg \gamma H$ , the tensor components are given approximately by

$$\mu \approx 1 \quad \kappa \approx \frac{4\pi M\gamma}{\omega}$$

<sup>1</sup> Prepared by C. L. Hogan and H. Solt, Jr., Fairchild Camera & Instrument Corp.

TABLE 5f-32. FARADAY ROTATION IN FERRITE MATERIALS  
A. Completely Filled Waveguide

Applied $H$ , oersteds	Rotation, deg/cm			
	$\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4^*$ ( $4\pi M_s = 1,500$ , $\lambda = 3.33$ cm)	$\text{MgFe}_2\text{O}_4^\dagger$ ( $4\pi M_s = 900$ , $\lambda = 3.2$ cm)	$\text{MgAl}_{0.4}\text{Fe}_{1.6}\text{O}_4^\ddagger$ ( $4\pi M_s = 540$ , $\lambda = 3.2$ cm)	$\text{MgAl}_{0.8}\text{Fe}_{1.2}\text{O}_4^\ddagger$ ( $4\pi M_s = 54$ , $\lambda = 3.2$ cm)
0.....	0	0	0	0
100.....	.....	.....	.....	1.1
200.....	.....	3	3	.....
400.....	.....	.....	6	.....
500.....	35	.....	7.4	.....
600.....	.....	9	.....	.....
1,000.....	80	14.3	.....	1.1
1,400.....	.....	14.3	7.4	.....
1,500.....	120	.....	.....	.....
2,000.....	123	.....	.....	.....
2,500.....	123	.....	.....	.....

B. Waveguide Containing Slender Cylinders at Saturation

Composition	Frequency, GHz	$4\pi M_s$ , gauss	Rotation, deg/cm	Loss, db/cm	Fig. of merit, deg/db
$\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Mn}_{0.2}\text{Fe}_{1.8}\text{O}_4^\ddagger$ .....	4.0§	3,840	17.5	0.9	19.5
$\text{Mg}_{1.5}\text{Mn}_{0.2}\text{Fe}_{1.5}\text{O}_4^\ddagger$ .....	4.0§	1,800	13.3	0.6	21.7
$\text{Mg}_{1.0}\text{Al}_{0.1}\text{Al}_{0.2}\text{Fe}_{1.9}\text{O}_4^\ddagger$ .....	4.0§	1,600	10.5	0.026	410
$\text{Ni}_{0.4}\text{Zn}_{0.6}\text{Mn}_{0.02}\text{Fe}_{1.9}\text{O}_4^\ddagger$ .....	11.2¶	3,850	9.4	0.013	730
$\text{Ni}_{0.7}\text{Zn}_{0.2}\text{Mn}_{0.1}\text{Fe}_{1.5}\text{O}_4^\ddagger$ .....	11.2¶	2,800	5.6	.....	2150
$\text{Mg}_{0.1}\text{Mn}_{0.02}\text{Al}_{0.2}\text{Fe}_{1.7}\text{O}_4^\ddagger$ .....	11.2¶	1,600	3.77	0.01+	370
Ferroxcube 4A**.....	24.0††	3,360	13.8	.....	.....
Ferroxcube 4B**.....	24.0††	4,400	28.0	.....	.....
Ferroxcube 4C**.....	24.0††	4,365	20.0	.....	.....
Ferroxcube 4D**.....	24.0††	3,470	9.8	.....	.....
Ferroxcube 4E**.....	24.0††	2,315	5.8	.....	.....

\* C. L. Hogan, *Bell System Tech. J.* **31**, 1-30 (1952).

† Roberts, F. F.: *J. phys. radium* **12**, 305 (1951).

‡ Private communication from J. P. Schafer, Bell Telephone Laboratories.

¶ 1.35-cm-diameter rods supported in polystyrene in 5-cm-diameter waveguide.

§ 0.355-cm-diameter rods supported in polyfoam in 1.9-cm-diameter waveguide.

\*\* A. A. T. M. van Trier, Thesis, Delft, 1953.

†† 1.0-mm-diameter rods.

where  $\gamma = ge/2$  MHz  $\approx 1.76 \times 10^7$  rad/sec-Oe, and  $M$  = intensity of magnetization of medium in cgs units. The rotation is then independent of frequency and field and is<sup>1</sup>

$$\theta = \frac{\sqrt{\epsilon}}{2c} 4\pi M \gamma$$

Table 5f-32 shows the Faraday rotation observed in a completely filled waveguide and in waveguides containing slender cylinders of ferrite along the waveguide axis.

<sup>1</sup> For further information, see C. L. Hogan, *Bell System Tech. J.* **31**, 1-30 (1952).

Measurements of completely filled waveguides are reliable only when the materials attenuate the wave appreciably because of the effects of internal reflections arising from the abrupt discontinuities at the ferrite-air interfaces. The data on the completely filled waveguide show the dependence of rotation upon magnetization as evidenced by the fact that the rotation approaches a limit as the applied field saturates the sample.

The data on the slender samples give the rotation at a field just sufficient to saturate the sample. The losses observed under these conditions are also shown along with the figure of merit given by the rotation in degrees per decibel of loss.

The dependence of Faraday rotation on magnetizing field is given<sup>1</sup> in Fig. 5f-38 for a slender sample.

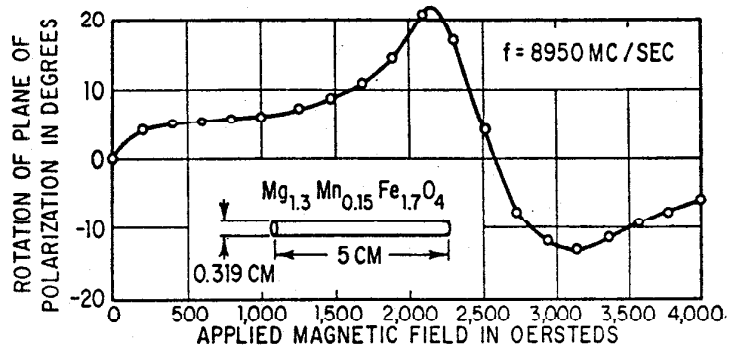


FIG. 5f-38. Faraday rotation in Mg-Mn ferrite as a function of the magnetic field strength<sup>1</sup>. Wavelength 3 cm; path length 5 cm.

Table 5f-33 giving data on semiconductors is included here because the phenomenon involved is closely related to the Faraday rotation in ferrites and can be described by an equation similar to that above when the tensor permeability is replaced by a tensor dielectric constant.

Additional data on solids, liquids, and gases will be found in Chap. 6.

**5f-14. Susceptibility.**<sup>2</sup> The atomic susceptibilities of the elements at room temperature are shown in Fig. 5f-39. Data are given in Table 5f-34 for materials which follow a Curie-Weiss law (see Sec. 5f-1) over a substantial temperature range.

The effective Bohr magnetons number per formula unit is given by the relation

$$\mu_{\text{eff}} = \left( 3k\chi_{\text{mole}} \frac{T - \theta}{N\beta^2} \right)^{\frac{1}{2}} = 2.83 \sqrt{C}$$

where  $\beta$  is the Bohr magneton, and  $C$  and  $\theta$  are constants of the Curie-Weiss law.

The chemical formulas as written are the simplest which include whole numbers only. In many cases, however, in order to make  $\mu_{\text{eff}}$  per formula unit correspond to the magnetic moment of an actual paramagnetic ion, the magnetic data and calculations refer to the formula multiplied by  $\frac{1}{2}$  or  $\frac{1}{3}$  or  $\frac{1}{4}$ . When this is so, the multiplying factor is indicated immediately after the formula thus:  $\text{Dy}_2\text{O}_3 \times \frac{1}{2}$ . If  $\mu_{\text{eff}}$  does correspond to the moment of a single dipole, then according to molecular field theory it is related to  $g$  and  $J$  by

$$\mu_{\text{eff}} = g \sqrt{J(J + 1)}$$

<sup>1</sup> Unpublished data by C. L. Hogan.

<sup>2</sup> Compiled by E. E. Anderson and A. Stelmach, Clarkson College of Technology.

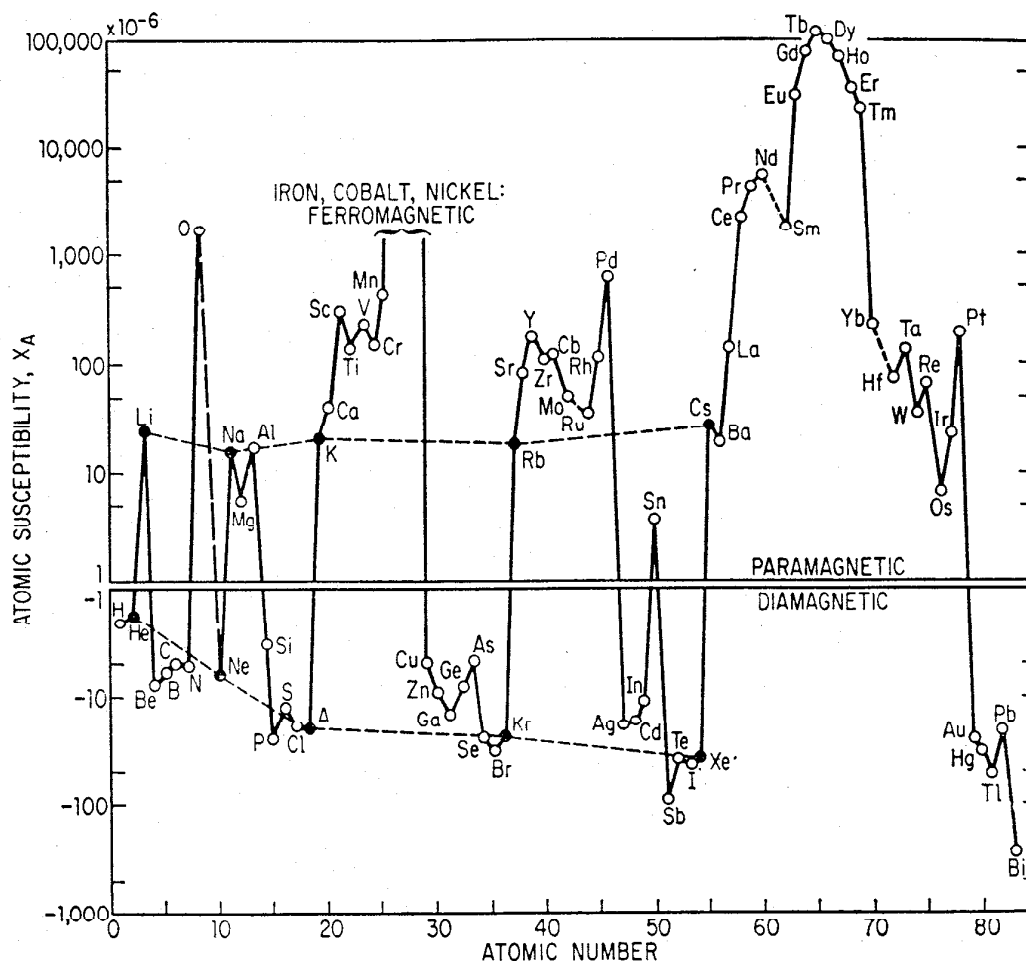


FIG. 5f-39. Atomic susceptibility of the elements at room temperature. Gd to Tm are ferromagnetic at low temperatures.

All data in Table 5f-34 for which references are not given are taken from G. Foëx.<sup>1</sup> Paramagnetic properties of certain ferrites above their Curie temperatures have been discussed by Néel,<sup>2</sup> who gives references to experimental work in this field. Also, further references to other materials which do not obey the Curie-Weiss law are to be found in Selwood<sup>3</sup> and in Staude.<sup>4</sup>

Electron-spin and orbital values for the rare-earth ions are given in Table 5f-3.

**5f-15. Very Low Temperature Data. Properties of Paramagnetic Salts.** The properties of a paramagnetic ion embedded in a crystal lattice are determined by a number of factors, viz., the level structure of the free ion, the strength and symmetry of the crystalline electric field, and the dipole-dipole and/or exchange interactions with neighboring ions. In general, ions with an odd number of unpaired ("magnetic") electrons will be found to have a number of doublets lying within  $\sim 1 \text{ cm}^{-1}$  of the ground level and all other levels at much higher energies. These latter are depopu-

<sup>1</sup> G. Foëx, "Constantes Sélectionnées: Diamagnétisme et Paramagnétisme," Tables de constantes et données numériques, Masson et Cie, Paris, 1957.

<sup>2</sup> L. Néel, *Ann. phys.* **3**(12), 137 (1948).

<sup>3</sup> P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, 1956.

<sup>4</sup> H. Staude, "Physikalisch-Chemisches Taschenbuch," vol. 2, p. 1624, Akademische Verlagsgesellschaft m.b.H., Leipzig, 1949.

TABLE 5f-33. FARADAY ROTATION IN SEMICONDUCTORS  
A. Silicon:\* Room Temperature,  $H$  in [100] Direction

Resistivity, ohm-cm	$V$ , min/(Oe)(cm)			
	$n$ -type, 9.6 GHz	$n$ -type, 35 GHz	$p$ -type, 9.6 GHz	$p$ -type, 35 GHz
1.....	-0.25	-1.1	0.12	0.3
2.9.....	-0.35	-0.8	0.12	0.2
5.....	-0.25	-0.4	0.09	0.15
10.....	-0.15	-0.2	0.04	
22.....	.....	-0.15	.....	0.04
40.....	.....	.....	.....	0.025

B. Germanium:† Room Temperature,  $H$  in [100] Direction, 24.9 GHz  
and Resistivity  $\rho$ , 3.8 ohm-cm

$H$ , oersteds	Rotation, deg/cm
3,200.....	70
6,400.....	130
8,300.....	160
11,800.....	210

\* Furdyna, J. K. and S. Broersma: *Phys. Rev.* **120**, 1995 (1960).

† Bouwknecht, A. and J. Volger: *Physica* **30**, 113 (1964).

lated at low temperatures, and one finds that Curie's law is followed in the liquid helium region unless the interactions are strong enough to modify this to the Curie-Weiss relation  $\chi = C(T - \theta')^{-1}$ . (Ions with an even number of unpaired electrons will usually have a singlet ground state and be nonmagnetic at low temperatures.)

Paramagnetic ions fall into separate groups within the Periodic Table, e.g., the  $3d$ ,  $4d$ , and  $5d$  transition series, the  $4f$  (rare-earth) and  $5f$  (transuranic) groups, wherein the general properties are determined by the relative strength of the electrostatic and spin-orbit interactions. Thus, in the case of the rare-earth ions the spin-orbit coupling  $\zeta L \cdot S$  is dominant,  $L$  and  $S$  are not uncoupled to a first approximation, and  $J$  remains a good quantum number, giving rise to  $(2J + 1)$ -fold degenerate multiplets. The crystal field splits these into doublets characterized (roughly) by  $\pm J_z$ . The latter may then be split by an external magnetic field. If the electrostatic energy is large, as in the case of the iron-group ( $3d$ ) ions, for example,  $L$  and  $S$  precess separately about the electric field axis and the levels are characterized by quantum numbers  $L_z$  and  $S_z$ . The splittings are generally so large that only the lowest orbital level is populated, and the remaining  $(2S + 1)$ -fold degeneracy may be partially lifted by the combined action of the electric field and the spin-orbit interaction, with splittings  $\sim 1 \text{ cm}^{-1}$ . The effect of crystalline fields of different symmetries on the iron-group ions is depicted in Fig. 5f-40.

A fictitious spin  $S$  is introduced to correspond to the multiplicity  $(= 2S + 1)$  of the lowest lying group of levels, and the "spin Hamiltonian" takes the form

$$\mathcal{H} = D[S_z^2 - \frac{1}{3}S(S + 1)] + \mu_B[g_{\parallel}\mathcal{O}_z S_z + g_{\perp}(\mathcal{O}_x S_x + \mathcal{O}_y S_y)] + A I_z S_z + B(I_x S_x + I_y S_y) \quad (5f-1)$$

TABLE 5f-34. MOLECULAR SUSCEPTIBILITIES, CURIE CONSTANTS, AND EFFECTIVE BOHR MAGNETON NUMBERS OF SOME PARAMAGNETIC MATERIALS\*  
( $\theta$  is constant in Curie-Weiss law)

Substance	$\chi_{\text{mole}} \times 10^6$ (20°C) (cgs units)	Range of validity of Curie- Weiss law, K	C	$\theta$ , K	$\mu_{\text{eff}}$
B <sub>2</sub> O <sub>3</sub> ·Fe <sub>2</sub> O <sub>3</sub> ·2MgO( $\times \frac{1}{2}$ ) [1]			2.7	-600	4.66
B <sub>2</sub> O <sub>3</sub> ·Fe <sub>2</sub> O <sub>3</sub> ·4CuO( $\times \frac{1}{2}$ ) [1]			2.6	-635	4.58
B <sub>2</sub> O <sub>3</sub> ·Fe <sub>2</sub> O <sub>3</sub> ·4CoO( $\times \frac{1}{2}$ ) [1]			5.0	-445	6.3
B <sub>2</sub> O <sub>3</sub> ·Fe <sub>2</sub> O <sub>3</sub> ·4NiO( $\times \frac{1}{2}$ ) [1]			4.2	-832	5.8
CeCl <sub>3</sub>	2,520	>80	0.787	-23	2.51
CeF <sub>3</sub>	2,240	>80	0.794	-62	2.52
Ce(NO <sub>3</sub> ) <sub>3</sub> ·5H <sub>2</sub> O	2,335	290 $\leftrightarrow$ 480	0.717	-17	2.39
CoBr <sub>2</sub> [24]	11,640	70 $\leftrightarrow$ 300	3.43	-20	5.24
Co(CN) <sub>2</sub>	~3,870		1.21	-9	3.11
CoCl <sub>2</sub> [23]		90-500	3.19	28	5.16
CoCr <sub>2</sub> S <sub>4</sub> ( $\times \frac{1}{2}$ ) [2]	13,060	<100	3.56	18.5	5.33
CoF <sub>2</sub> [22]	4,700	>500	2.08	-410	4.08
CoF <sub>2</sub> [22]	8,660	50 $\leftrightarrow$ 300	2.90	-50	5.15
CoGeO <sub>4</sub> ( $\times \frac{1}{2}$ ) [35]	13,100	>300	2.75	90	4.70
CoI <sub>2</sub> [24]	10,880	50-300	3.12	0	5.12
Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O [3]	9,050	>8	2.58	8	4.58
CoO [4], [25]	5,235	>300	3.23	330	5.25
CoS <sub>2</sub> [26]	3,520	>155	0.49	161	1.85
CoSO <sub>4</sub> [27]	10,200	95-300	3.36	-47	5.65
CoSO <sub>4</sub> ·7H <sub>2</sub> O	0,780	77-350	2.91	-14	5.03
CoTiO <sub>3</sub> [5]	12,400		3.72	-9.2	5.64
CrBr <sub>3</sub> [6]	7,700	>100	1.94	51	3.94
CrCl <sub>2</sub> [28]	7,330	>225	2.97	-116	4.88
CrCl <sub>3</sub> [6]	6,860	210-690	1.82	24	3.82
CrF <sub>3</sub> [6]	4,450	>65	1.90	-124	3.90
CrI <sub>3</sub> [6]	6,700	>100		70	4.03
CrS [2]	1,610	>560	2.6	$\approx$ -800	4.6
Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ( $\times \frac{1}{2}$ ) [3]	10,500	>11	2.94	11	4.89
Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·8H <sub>2</sub> O( $\times \frac{1}{2}$ ) [3]	10,600	>19	2.88	19	4.85
Cr(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O [3]	5,320	>20	1.41	20	3.43
CrK(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O	6,320		1.84	0	3.84
CuCl <sub>2</sub> [34]	1,340	155-670	0.457	-78	1.97
CuS [7]		<100	0.04	-25	0.58
CuSO <sub>4</sub> [34]	1,340	90 $\leftrightarrow$ 500	0.50	-67	2.10
CuSO <sub>4</sub> ·5H <sub>2</sub> O	1,570		0.46	-0	1.92
DyNi <sub>2</sub> [36]			13.5	23	10.4
Dy <sub>2</sub> O <sub>3</sub> ( $\times \frac{1}{2}$ )	43,200		13.6	-24	10.5
DyP [8]			13.0	9	10.22
Dy <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·8H <sub>2</sub> O( $\times \frac{1}{2}$ )	$\approx$ 45,000		13.74	-5	10.5
ErNi <sub>2</sub> [36]			11.0	-11	9.37
Er <sub>2</sub> O <sub>3</sub> ( $\times \frac{1}{2}$ )	38,600		11.6	-8	9.65
Er <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ( $\times \frac{1}{2}$ )	28,700		8.24	-2	8.12
Er <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·8H <sub>2</sub> O( $\times \frac{1}{2}$ )	36,500		11.18	-6	9.46
EuCl <sub>2</sub>	26,600		7.80	-1	7.90
Eu <sub>2</sub> O <sub>3</sub> ( $\times \frac{1}{2}$ )	5,550		3.26	-294	5.11
EuS	23,800		6.81	6	7.38
EuSO <sub>4</sub>	25,800		7.64	-4	7.81
FeCl <sub>2</sub> [29]	13,200	90 $\leftrightarrow$ 300	3.60	48	5.37
FeCl <sub>2</sub> ·4H <sub>2</sub> O	12,060		3.37	12	5.18
FeCl <sub>3</sub>	13,900		3.93	10	5.6
FeCr <sub>2</sub> S <sub>4</sub> ( $\times \frac{1}{2}$ ) [2]	4,100	>300	2.22	-240	1.22
FeF <sub>2</sub>	9,460		3.88	-117	5.57
Fe <sub>2</sub> GeO <sub>4</sub> ( $\times \frac{1}{2}$ ) [35]	11,500	>100	3.63	-15	5.40
FeSO <sub>4</sub> [30]	12,400	40 $\leftrightarrow$ 300	3.60	-30.5	5.20
FeSO <sub>4</sub> ·7H <sub>2</sub> O [31]	11,930	80 $\leftrightarrow$ 300	3.52	-1.0	5.22
Fe(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	13,100		3.78	2	5.49
Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ( $\times \frac{1}{2}$ )	12,100		4.3	-61	5.9
Fe(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O	14,900	>20	4.2	0	5.8
Fe <sub>3</sub> [Fe(CN) <sub>6</sub> ] <sub>2</sub> ·14.5H <sub>2</sub> O( $\times \frac{1}{2}$ ) [9]	14,000	>77	3.92	14.7	5.6
FeTiO <sub>3</sub> [5], [32]	14,560	80 $\leftrightarrow$ 290	3.37	23	5.46
GdAs [10]		100 $\leftrightarrow$ 500	7.8		$\approx$ 7.9
GdB [10]		100 $\leftrightarrow$ 500	7.8		$\approx$ 7.9
GdCl <sub>3</sub>	24,700		7.51	-11	7.75
GdLa [11]		>20.4	30.0	-3 $\pm$ 2	
GdNi <sub>2</sub> [36]			7.62	78	7.82
Gd <sub>2</sub> O <sub>3</sub> ( $\times \frac{1}{2}$ )	24,500		7.61	-18	7.80
GdP [8]	28,700	100-500	7.45	39	7.72
GdS [10]		100 $\leftrightarrow$ 500	7.8		$\approx$ 7.9
Gd <sub>2</sub> S <sub>4</sub> ( $\times \frac{1}{2}$ ) [12]	23,400	>77	7.02	0	$\approx$ 7.50 $\leftrightarrow$ 7.55
GdSb [10]		100 $\leftrightarrow$ 500	7.8		$\approx$ 7.9
GdSe [10]		100 $\leftrightarrow$ 500	7.8		$\approx$ 7.9
Gd <sub>2</sub> Se <sub>4</sub> ( $\times \frac{1}{2}$ ) [12]	27,500	>77	8.24	0	$\approx$ 8.14



TABLE 5f-34. MOLECULAR SUSCEPTIBILITIES, CURIE CONSTANTS, AND EFFECTIVE BOHR MAGNETON NUMBERS OF SOME PARAMAGNETIC MATERIALS\* (Continued)

Substance	$\chi_{\text{mole}} \times 10^6$ (20°C) (cgs units)	Range of validity of Curie- Weiss law, K	C	$\theta$ , K	$\mu_{\text{eff}}$
Gd <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (× 1)	26,600		7.81	-0.4	7.90
Gd <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·8H <sub>2</sub> O (× 1)	27,500		8.11	-2	8.06
GdTe [10]		100 ← 500	7.8		7.9
HCrO <sub>2</sub> [13]	3,300		1.934	-279.6	3.92
HoNi <sub>2</sub> (× 1/3) [36]			13.7	12	10.5
Ho <sub>2</sub> O <sub>3</sub> (× 1/3)	44,800		13.7	-14	10.5
Ho <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (× 1/3)	45,900		13.8	-8	10.5
Ho <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·8H <sub>2</sub> O (× 1/3)	44,300		13.6	-7	10.43
KFe[Fe(CN) <sub>6</sub> ]·1.9H <sub>2</sub> O [9]		>77	4.05	22	5.7
K <sub>2</sub> MnO <sub>4</sub>	1,270		0.383	-7	1.75
Li <sub>2</sub> NiF <sub>4</sub> [12]		77 ← 473			3.18
MgCr <sub>2</sub> O <sub>4</sub> (× 1/3) [35]	2,800	>100	1.86	-350	3.84
MgV <sub>2</sub> O <sub>4</sub> (× 1/3) [35]	1,400	>50	1.47	-750	3.43
MnBr <sub>2</sub>	14,000	70 ← 180	4.26	-2	5.84
MnCO <sub>3</sub>	≈ 11,500		3.93	-40	5.61
MnCl <sub>2</sub> [23]	14,500	2 ← 800	4.17	3	5.78
MnCo <sub>2</sub> O <sub>4</sub> (× 1/3) [2]	2,820	>300	1.91	-380	3.91
MnCr <sub>2</sub> S <sub>4</sub> (× 1/3) [2]	8,200	>300	2.54	-10	4.51
MnF <sub>2</sub> [33]	10,730	76 ← 300	≈ 4.10	82	5.98
MnF <sub>3</sub> [14]			3.01	8	4.91
MnI <sub>2</sub>	14,800	35 ← 200	4.21	-4	5.80
MnO	5,040	>120	4.90	-680	6.26
Mn <sub>2</sub> O <sub>3</sub> (× 1/3)	7,080		3.40	-188	5.21
MnO <sub>2</sub>	≈ 2,300		1.80	-480	3.78
Mn(OH) <sub>2</sub>	≈ 13,700	200 ← 300	4.60	20	5.5
Mn <sub>2</sub> P <sub>2</sub> O <sub>7</sub> (× 1/3)	14,400	195 ← 770	4.58	-23	6.05
MnRh [15]	≈ 790 (4.2°K)	170 ← 700		≈ -260°K	
MnSO <sub>4</sub>	13,960	77 ← 660	4.34	-22	5.88
MnTiO <sub>3</sub> [5]			4.36	-219	
NdCl <sub>3</sub> [16]		290 ← 570	1.861	-57.4	3.87
NdF <sub>3</sub>	5,020	>155	1.76	-56	3.75
NdNi <sub>2</sub> (× 1/3) [36]			1.75	10	3.74
Nd <sub>2</sub> O <sub>3</sub> (× 1/3)	4,700		1.53	32	3.50
Nd <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (× 1/3)	5,070		1.70	-42	3.69
Nd <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·8H <sub>2</sub> O (× 1/3)	5,390		1.82	-44	3.81
NiCl <sub>2</sub>	6,250	>340	1.50	28	3.47
		<510	1.37	71	3.32
NiF <sub>2</sub>	3,450	100 ← 300	1.34	-97	3.27
Ni <sub>2</sub> GeO <sub>4</sub> (× 1/3) [35]	4,370	>100	1.31	0	3.24
Ni(NO <sub>2</sub> ) <sub>2</sub> ·6H <sub>2</sub> O [3]	5,700	>21	1.01	21	2.86
NiTiO <sub>3</sub> [5]			1.24	-11	3.15
PrCl <sub>3</sub> [16]		285 ← 700	1.69	-29.4	3.69
PrNi <sub>2</sub> (× 1/3) [36]			1.60	4	3.57
Pr <sub>2</sub> O <sub>3</sub> (× 1/3)	4,450		1.62	-71	3.60
Pr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (× 1/3)	≈ 4,900	65 ← 370	1.64	-44	3.62
TbNi <sub>2</sub> (× 1/3) [36]			12	35	9.82
TbP [8]			10.8	5	9.28
Tb <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·8H <sub>2</sub> O (× 1/3)	37,500		11.86	-16	9.74
TlMnF <sub>3</sub> [17]		>150	4.87	148	6.25
TmAs [18]		>≈ 20			≈ 7.6
TmNi <sub>2</sub> (× 1/3) [36]			0.04	0	7.23
Tm <sub>2</sub> O <sub>3</sub> (× 1/3) [19]		80 ← 980	7.2		7.56
TmP [18]		>≈ 20	7.2		≈ 7.6
TmSb [18]		>≈ 20	7.2		≈ 7.6
Tm <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (× 1/3)	20,800		6.33	-11.7	7.11
UCl <sub>4</sub> [20]			1.35	-62	3.29
UBr <sub>4</sub> [20]			1.21	-35	3.12
UBr <sub>3</sub> [20]			1.35	25	3.29
UCl <sub>3</sub> [20]			1.15	-29	3.03
UF <sub>4</sub> [20]			1.36	-147	3.30
UI <sub>3</sub> [20]			1.38	5	3.31
KUF <sub>6</sub> [21]			1.30	-122	3.30
K <sub>2</sub> UF <sub>6</sub> [21]		>198	1.47	-108	3.45
CaUF <sub>6</sub> [21]			1.31	-101	3.25
Na <sub>3</sub> UF <sub>7</sub> [21]			1.45	-290	3.40
UO <sub>2</sub>	2,240		1.06	-185	2.92
U <sub>3</sub> O <sub>8</sub> (× 1/3)	525		0.24	-170	1.39
U(SO <sub>4</sub> ) <sub>2</sub>	3,060		1.32	-140	3.25
Yb <sub>2</sub> O <sub>3</sub> (× 1/3)	6,700		2.43	-68	4.40
Yb <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·8H <sub>2</sub> O (× 1/3)	≈ 8,600		2.92	-42	4.83
ZnCo <sub>2</sub> O <sub>4</sub> (× 1/3) [2]	625	>100	0.21	-20	1.3
ZnCr <sub>2</sub> S <sub>4</sub> (× 1/3) [2]	5,750	>100	1.67	+10	3.66

\* Compiled by E. E. Anderson and A. Stelmach, Clarkson College of Technology.

## References for Table 5f-34

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for axial symmetry. Here,  $D$ ,  $A$ , and  $B$  are constants and  $I$  is the nuclear spin.  $D$  is determined by the crystalline electric field, and  $A$  and  $B$  by the hyperfine coupling.  $g_{\parallel}$  and  $g_{\perp}$  are the spectroscopic splitting factors for the  $z$  direction (parallel to the crystal-field symmetry axis) and in the  $xy$  plane, respectively. Terms representing the nuclear electric quadrupole interaction (for  $I > \frac{1}{2}$ ) and the direct coupling of the nuclear magnetic moment with the external field have been omitted from Eq. (5f-1).

The parameters in the spin Hamiltonian are determined by electron paramagnetic resonance (epr) spectroscopy, and the correctness of the assumed crystal field symmetry can be checked by studying the angular dependence of the resonance pattern. Frequently the line width due to magnetic dipole interaction is comparable with the fine structure and hyperfine structure (hfs) separations. Then the established practice is to dilute the subject salt with an isomorphous diamagnetic salt. In most cases the electric field acting on the ion remains unaltered, but there are instances of drastic modifications occurring.

If all the ions in the crystal have the same symmetry axis, the susceptibility will be given by the formulas [1].

$$\begin{aligned} \chi_{\parallel} &= Ng_{\parallel}^2 \mu_B^2 \frac{S(S+1)}{3kT} \left[ 1 - \frac{D(2S-1)(2S+3)}{15kT} \right] \\ \chi_{\perp} &= Ng_{\perp}^2 \mu_B^2 \frac{S(S+1)}{3kT} \left[ 1 + \frac{D(2S-1)(2S+3)}{30kT} \right] \end{aligned} \quad (5f-2)$$

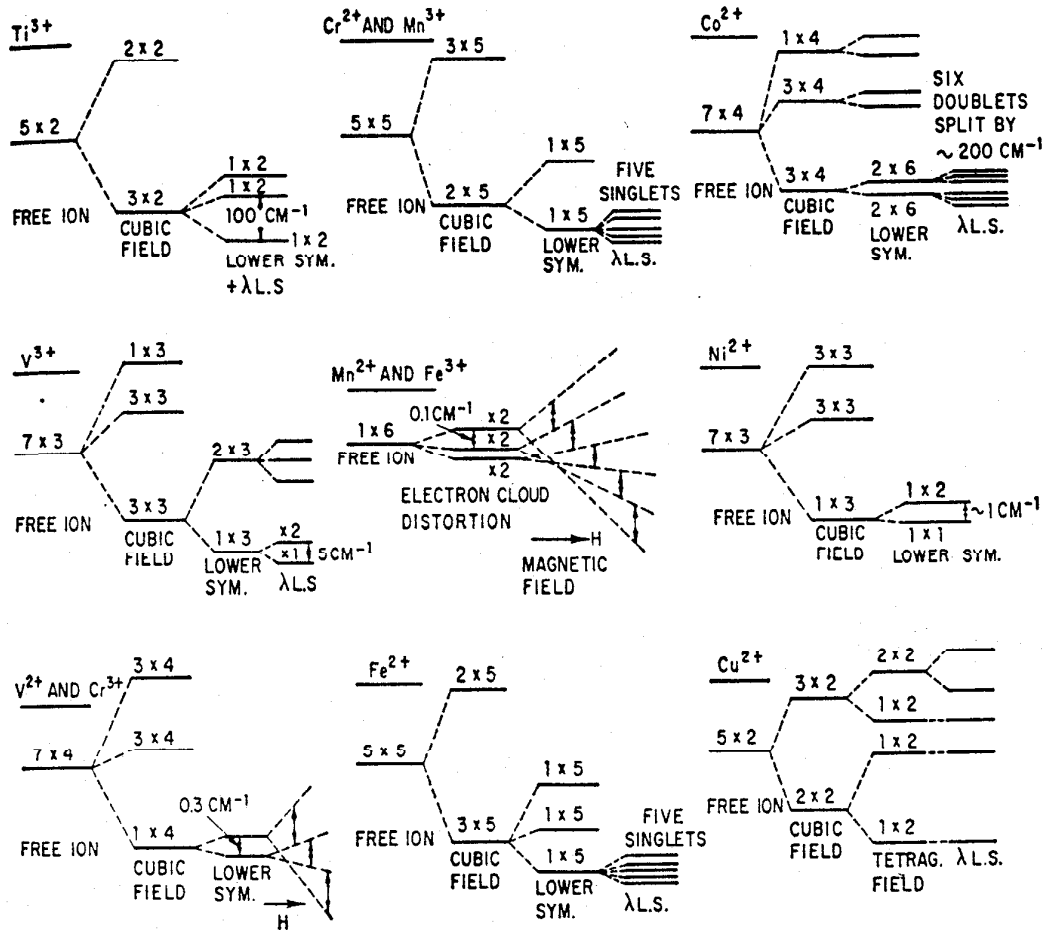


FIG. 5f-40. Iron transition group. Splitting of levels. (Not to scale.)

Here,  $N$  is Avogadro's number,  $k$  is the Boltzmann constant, and  $\mu_B$  is the Bohr magneton value.  $D/k$  is measured in kelvins, and  $N\mu_B^2/3k$  is very closely equal to  $\frac{1}{8}$  for 1 g ion (0.12506). If there are groups of ions with different symmetry axes, these expressions can be used to calculate the susceptibility by averaging over the groups, and for the particular case of a powder the  $D$  term vanishes.

The Stark splitting introduces a contribution to the specific heat which, for  $D \ll kT$ , is given by

$$\frac{c_v T^2}{R} = b_v = \frac{D^2}{45} S(S+1)(2S-1)(2S+3) \quad (5f-3a)$$

and the hfs contribution is

$$\frac{c_n T^2}{R} = b_n = \frac{1}{9} (A^2 + 2B^2) S(S+1) I(I+1) \quad (5f-3b)$$

where  $A$ ,  $B$ , and  $D$  are in kelvins, and  $R$  is the molar gas constant. If these parameters are given in  $\text{cm}^{-1}$ , the above expressions for  $b$  are to be multiplied by  $(hc/k)^2 = 1.4388^2 = 2.070$ .

Magnetic dipole interaction also gives rise to a term in the specific heat varying as  $T^{-2}$  in high-temperature approximation. For isotropic ions [2] this is

$$\frac{c_i T^2}{R} = b_i = fC^2$$

where  $C$  is the Curie constant per  $\text{cm}^3$ , and  $f$  is a factor dependent upon the lattice arrangement of the magnetic ions, e.g., 21.6 for the alums and 26.5 for the Tutton salts. The theory has also been worked out for the case of anisotropic crystals [3].

At high temperatures the effects of interactions on the specific heat are additive, and  $b = b_e + b_n + b_i$ . The magnitudes of the dipolar and (especially) the crystal field interactions, however, are such that  $cT^2$  will not remain constant as  $T$  falls below 1 K.

1. *Titanium Cesium Alum.*  $\text{Ti}_2(\text{SO}_4)_3 \cdot \text{Cs}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ ; gram-ionic weight, 589.14; density, 2.019;  $\text{Ti}^{3+}$ ;  $3d^1$ ;  ${}^2D_3$ .

This salt is of interest in that it provides an example of a  $3d^1$  ion in the iron-group series of paramagnetics, but its chemical instability renders it difficult to work with.

In a crystalline electric field of cubic symmetry, the  ${}^2D$  state is split into a lower orbital triplet and an upper orbital doublet. The triplet, with twofold spin degeneracy, is split into three Kramers doublets by the action of the trigonal component of the crystal field and spin-orbit coupling. The separations are only a few hundred  $\text{cm}^{-1}$ . At low temperatures only one doublet is populated, with effective  $S = \frac{1}{2}$ . Owing to the nearness of two higher states, the  $g$  value departs markedly from 2 and is anisotropic while the spin-lattice relaxation time is short and highly temperature dependent. In the alums, the overall cubic symmetry is preserved by the fact that there are four magnetic ions in the unit cell, the individual trigonal axes forming the body diagonals of a cube.

In order to account for their observations  $g_{\parallel} = 1.25$ ,  $g_{\perp} = 1.14$ , Bleaney and others [4] found it necessary to invoke the hypothesis of the  $d$  electron taking part in  $\pi$  bonding to the water molecules and to introduce an "orbital reduction factor." There will then be an excited state within a few tens of  $\text{cm}^{-1}$  of the ground state, which would explain the anomalous behavior of the susceptibility found by van den Handel [5]. Benzie and Cooke [6] found for a powder specimen:  $C = 0.118$  emu/g-ion;  $g = 1.12$  (and estimated  $g_{\parallel} = 1.40$ ,  $g_{\perp} = 0.96$ );  $bR/C = 2.7 \times 10^4$  ( $\pm 10$  percent); and hence  $b = 3.9 \times 10^{-5}$  where  $b = b_e + b_n + b_i$ . By dilution experiments they showed that nuclear hfs in the odd isotopes contributes  $0.4 \times 10^{-5}$  to  $b$ . Magnetic dipole interaction accounts for  $0.3 \times 10^{-5}$ , and the balance of  $3.2 \times 10^{-5}$  must be due to exchange. The spin-lattice relaxation time varied as  $T^{-7.5}$  between 0.9 and 1.3 K, being  $3.3 \times 10^{-4}$  sec at 1 K. The excited doublets were estimated to lie at 174 and 364  $\text{cm}^{-1}$ , respectively.

Adiabatic demagnetization experiments [7] gave  $(S/R)_{T_c} = 0.22$ , for  $\mathcal{B}/T = 0.26$  T/K; here  $S$  is the entropy, ignoring the nuclear contribution. The odd isotopes  $\text{Ti}^{47}$  ( $I = \frac{5}{2}$ , 7.75 percent abundant) and  $\text{Ti}^{49}$  ( $I = \frac{7}{2}$ , 5.51 percent) will contribute  $0.253R$  to the entropy.

2. *Chromic Potassium Alum.*  $\text{Cr}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ ; gram-ionic weight, 499.42; density, 1.83;  $\text{Cr}^{3+}$ ;  $3d^3$ ;  ${}^4F_3$ .

A cubic field leaves an orbital singlet lowest, some  $10^4$   $\text{cm}^{-1}$  below the first triplet. This spin quadruplet splits into two Kramers doublets in any field of lower symmetry.  $g = 1.98$ . Paramagnetic resonance experiments by Bleaney [8] indicate two distinct values of the splitting  $\delta$  below 160 K, a feature which is not understood. The spectrum intensities indicated roughly equal fractions for the two sets of ions, and Bleaney found it necessary to postulate the existence of a third set with a very small splitting to account for the observed value of  $b$ . Vilches and Wheatley [9] made calorimetric measurements down to 0.017 K—using a thermometer of CMN (cerous magnesium nitrate, q.v.)—and found that the specific heat down to 0.07 K could be accurately accounted for using the Bleaney assignments but somewhat different percentages:  $\delta_1 = 0.27$   $\text{cm}^{-1}$ , 28 percent;  $\delta_2 = 0.15$   $\text{cm}^{-1}$ , 28 percent;  $\delta_3 = 0.035$   $\text{cm}^{-1}$ , 44 percent.

The single odd isotope of chromium,  $\text{Cr}^{53}$  ( $I = \frac{3}{2}$ ), has an abundance of 9.54 percent and a small nuclear moment,  $-0.47$  nuclear magneton. Bleaney and Bowers [10]

achieved resolution of the hfs in paramagnetic resonance studies of diluted (with aluminum) chromic potassium selenate alum enriched in  $\text{Cr}^{53}$ . Their value for  $A$ ,  $18.5 \times 10^{-4} \text{ cm}^{-1}$ , indicates that the associated entropy,  $0.0954 \times R \ln 4$  or  $0.132R$ , will noticeably affect the properties of the chrome alums in the region 0.002 to 0.2 K, and this probably accounts for the fact that the dipolar specific-heat anomaly in this salt is found not in the region of  $S/R \sim \ln 2$ , but well below.

Adiabatic demagnetization experiments lead to an rms value of  $\delta$ , and the results of various investigators [11-14] can be summarized by  $\delta/k = 0.258 \pm 0.008 \text{ K}$ ; hence  $b_e = 0.017$ . With  $b_i = 0.001$ , one obtains  $b = 0.018$ . From direct measurements Kapadnis [15] finds, for the range 1 to 4 K,  $b = 0.0162$ .

Daniels and Kurti [12] measured the course of entropy with absolute temperature down to 0.007 K;  $T_c = 0.0115 \text{ K}$  at  $S/R = 0.40$  (neglecting hfs—see above);  $\mathcal{B}/T = 1.6 \text{ T/K}$ . Further measurements by Beun et al. [14] are in quite good agreement with these results; hence it is probable that the unusually low temperatures estimated by deKlerk et al. [16] were in error. As Durieux et al. showed [17] by precise measurements in the liquid-helium region, this salt actually obeys the Curie-Weiss law, with  $\theta' = -0.037 \text{ K}$ . They also show that a more accurate formula which takes account of the crystal field (and is valid down to  $\sim 0.3 \text{ K}$ ) is  $\chi = C(T + 0.00304T^{-1} - \theta)^{-1}$ , and here  $\theta = -0.033 \text{ K}$ . For still lower temperatures a graphical function is given for calculating the diminution of  $\theta$  (i.e., of the exchange interaction) with decreasing  $T$ .

3. *Chromic Methylammonium Alum.*  $\text{Cr}_2(\text{SO}_4)_3 \cdot (\text{CH}_3\text{NH}_2)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ ; gram-ionic weight, 492.39; density, 1.645;  $\text{Cr}^{3+}$ ;  $3d^3$ ;  ${}^4F_3$ .

The discussion is the same as for the potassium salt except that here there is a unique value for the splitting [8]. Adiabatic demagnetization experiments give  $\delta/k = 0.270 \pm 0.005 \text{ K}$  [18-21] corresponding to  $b_e = 0.0182 \text{ K}^2$  which is significantly greater than the 0.245 K from the epr results.  $b_i = 8.6 \times 10^{-4} \text{ K}^2$ . Baker made a detailed reinvestigation [22] and showed that there exists a small rhombic distortion of the crystal field. This adds a term  $+E(S_x^2 - S_y^2)$  to the Hamiltonian of Eq. (5f-1) and brings the derived value of  $\delta/k$  [ $\delta = 2(D^2 + 3E^2)^{1/2}$ ] up to 0.255 K, with  $g = 1.976$ .  $D = 0.087$ ,  $E = 0.009 \text{ cm}^{-1}$ . Thus there is still a discrepancy of some 5 percent in  $\delta$  which remains unexplained.

Despite the greater atomic volume of this salt ( $299 \text{ cm}^3$ ) compared with that of the potassium alum ( $272 \text{ cm}^3$ ), its Curie temperature is 50 percent higher, viz., 0.016 K [21].  $(S/R)_{T_c} = 0.53$  for  $\mathcal{B}/T \approx 1.34 \text{ T/K}$ .

Durieux et al. [17] investigated departures from Curie's law for this salt as well as for the potassium alum (q.v.). They obtained  $\theta' = -0.013$  and, in the formula  $\chi = C[T + 0.00279T^{-1} - \theta]^{-1}$ ,  $\theta = -0.010 \text{ K}$ .

4. *Vanadous Ammonium Sulfate.*  $\text{VSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ ; gram-ionic weight, 387.26; density, ;  $\text{V}^{2+}$ ;  $3d^3$ ;  ${}^4F_3$ . (Blank space indicates density is not yet known.)

The discussion is the same as for  $\text{Cr}^{3+}$ . The  $\text{V}^{2+}$  ion oxidizes easily but is somewhat more stable in a zinc-diluted crystal such as is required for narrow epr lines. Preparation [23,24] is conducted in a chilled reducing solution and inert atmosphere. The spin Hamiltonian parameters are [25]:  $g_{\parallel} = 1.951$  and probably isotropic;  $D = 0.158$ ;  $E = 0.049$ ,  $A (= B) = 0.0088 \text{ cm}^{-1}$ . Vanadium is 99.8 percent  $\text{V}^{51}$ , with  $I = \frac{7}{2}$ . For  $D \gg E$  and  $A$  it is shown [26] that  $b = D^2 + 3E^2 + 105A^2/16$  ( $D$ ,  $E$ , and  $A$  in kelvins) = 0.056.

5. *Ferric Ammonium Alum.*  $\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ ; gram-ionic weight, 482.21; density, 1.71;  $\text{Fe}^{3+}$ ;  $3d^5$ ;  ${}^6S_5$ .

The free ion being in an  $S$  state, interaction with the crystalline electric field is small. The sixfold degenerate level is split by a cubic field into a doublet and a quadruplet. A distortion of trigonal symmetry will result in three doublets. Specific-heat data derived from paramagnetic relaxation measurements [27] suggested three equally

spaced doublets, of overall splitting 0.23 K. This picture was substantiated by Meijer's analysis [28] of resonance measurements on aluminum-diluted iron alum [29]. Recent low-temperature specific-heat data [9] similarly analyzed [30] strongly suggest, however, that the trigonal component is negligibly small!

Elucidation of the properties by paramagnetic resonance studies has proved to be difficult. In the concentrated salt, magnetic interactions cause a large line width, comparable to the fine structure. Even upon dilution with the corresponding aluminum alum the resolution remains rather poor, probably owing to inhomogeneity as the splitting varies with degree of dilution.

Vilches and Wheatley [9] measured the specific heat down to 0.02 K and observed a pronounced  $\lambda$ -type anomaly at 0.0260 K. Cooke, Meyer, and Wolf [31] compared  $T^*$  with  $T$  as indicated by CMN, using a novel compound specimen technique, over the range 0.05 to 1 K. As noted above [9], these results when combined with the  $S - T^*$  data of Kurti, Squire, and Simon reported in [32] agreed with the  $S - T$  derivation of Vilches and Wheatley where overlap exists.  $T_c = 0.026$  K at  $S/R = 0.69$ . Steenland et al. [33] found  $(S/R)_{T_c} = 0.65$  at  $\mathcal{B}/T = 1.15$  T/K.

There are also fairly wide variations in the values reported for  $b$ , viz., 0.0123 [34], 0.0128 [11], 0.0135 [15,35], and 0.0143 [27]. The spread may be due to imperfect crystals in view of the sensitivity of the crystal field splitting to dilution. In the dilution range 3:1 to 6:1 (Al:Fe),  $b$  actually doubles; at 20:1 it is back to that of the pure ferric salt [35,36].

6. *Ferric Methylammonium Alum.*  $\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{CH}_3\text{NH}_3)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ ; gram-ionic weight, 496.24; density, 1.659;  $\text{Fe}^{3+}$ ;  $3d^5$ ;  ${}^6S_{5/2}$ .

The epr spectrum was found by Bleaney and Trenam [37] to be very complex, largely owing to the excitation of "forbidden" transitions as the measuring frequency was comparable in (energy) magnitude with the zero-field splittings. Their general Hamiltonian for the alums contains a cubic term and trigonal terms of second and fourth degree:

$$\begin{aligned} \mathcal{H} = g\mu_B\mathcal{B} \cdot \mathbf{S} \\ + \frac{a}{6} \left[ S_\xi^4 + S_\eta^4 + S_\zeta^4 - \frac{S}{5} (S+1)(3S^2 + 3S - 1) \right] + D \left[ S_z^2 - \frac{S}{3} (S+1) \right] \\ + \frac{F}{180} [35S_z^4 - 30S(S+1)S_z^2 + 25S^2 - 6S(S+1) + 3S^2(S+1)^2] \end{aligned}$$

Here,  $\xi$ ,  $\eta$ ,  $\zeta$  form a set of mutually perpendicular axes, with respect to which the  $z$  axis is the (111) direction. The specific heat can be computed from

$$b = \frac{56}{9} D^2 + 2a^2 - \frac{11}{27} F(2a - F)$$

The term in  $F$  is always very small and detectable only in high-resolution circumstances. Zero-field splittings were found to be  $0.393 \text{ cm}^{-1}$  and  $0.740 \text{ cm}^{-1}$ . These are equal to  $2D + \frac{5}{3}a$  and  $4D - \frac{4}{3}a$ , if one assumes that  $a \ll D$ . Then  $D = -0.188 \text{ cm}^{-1}$  and  $a = -0.010 \text{ cm}^{-1}$ . Cooke et al. [38] measured the specific heat between 0.17 and 20 K and showed that the  $\pm \frac{1}{2}$  level lies lowest.  $b = 0.455$ . Their data were confirmed and extended to about 0.1 K by Croft and Exell [39]. This substance should be very useful as an inexpensive substitute for gadolinium sulfate (q.v.) as a refrigerant in the range 0.1 to 1 K.

7. *Manganous Ammonium Sulfate.*  $\text{MnSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ ; gram-ionic weight, 391.24; density, 1.83;  $\text{Mn}^{2+}$ ;  $3d^5$ ;  ${}^6S_{5/2}$ .

The free ion being in an  $S$  state, the interaction with the crystalline electric field is small in this Tutton salt. Epr experiments on a zinc-diluted salt [40] showed

that  $g = 2.000$  and is isotropic to about 1 part in  $10^4$ . The hfs is surprisingly large and has received an explanation from Abragam and Pryce [41] who postulate a distortion of the nominally spherical electron-cloud distribution by the electric field.  $D$  ( $\sim 0.028 \text{ cm}^{-1}$ ) and  $E$  ( $\sim 0.005 \text{ cm}^{-1}$ ) are sensitive to temperature and dilution, but  $A$  ( $= 0.009 \text{ cm}^{-1}$ ) is not.  $\text{Mn}^{55}$ , with  $I = \frac{5}{2}$ , is 100 percent abundant. The  $z$  axes of the two ions in the unit cell are inclined to each other at an angle  $2\alpha$ , where  $\alpha = 32 \text{ deg}$ . Neglecting the effects of exchange, the susceptibility can be calculated from  $\chi = \chi_{\parallel} \cos^2 \beta + \chi_{\perp} \sin^2 \beta$  and Eq. (5f-2) with  $\beta = 32 \text{ deg}$ ,  $90 \text{ deg}$ , and  $58 \text{ deg}$  for the  $K_1$ ,  $K_2$ , and  $K_3$  axes, respectively.

The low-temperature specific heat has been measured as a function of dilution [35] in order to separate the various contributions to  $b = 0.032 \text{ K}^2$ . Dipole-dipole interaction accounts for 0.0106, Stark splitting plus hfs for 0.016, and an appreciable exchange interaction must be present to account for the balance. Other values reported for  $b$  range from 0.0306 [31] to 0.034 [42].

A number of adiabatic demagnetization studies have been made, [31,32,34,43,45]. The entropy vs. temperature measurements of Miedema et al. [45] below the Curie point ( $T_c = 0.14 \text{ K}$  at  $S/R = 1.25$ ) can be added quite satisfactorily to those of Cooke and Hull [32] made largely above the Curie point ( $T_c = 0.14 \text{ K}$ ,  $S/R = 1.27$ ). In this work, it was found that the sign of  $D$  is negative, contradicting the conclusions drawn in ref. 40.  $\theta'$  should then range from  $+0.035 \text{ K}$  ( $K_1$ ) to  $-0.03 \text{ K}$  ( $K_2$ ) (and zero for a powder), modified by any exchange contribution. The results of Durieux et al. [17], however, from measurements in four (unspecified) directions range from  $+0.079$  to  $-0.032 \text{ K}$ . Recent specific heat measurements [9] between 0.1 and 1 K yield an entropy-temperature curve qualitatively in agreement with those mentioned above but displaced toward higher temperatures. The  $\lambda$ -type anomaly was located at 0.173 K and investigated in detail;  $S_c/R = 1.27$ .

8. *Cobaltous Ammonium Sulfate*.  $\text{CoSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ ; gram-ionic weight, 395.25; density, 1.902;  $\text{Co}^{2+}$ ;  $3d^7$ ;  ${}^4F_{3/2}$ .

This is a Tutton salt. In a cubic field the sevenfold degenerate orbital level is split into two triplets and a singlet, with one triplet lying lowest. The latter, with fourfold spin degeneracy, is then split into Kramers doublets by the combined effect of the spin-orbit coupling and fields of lower symmetry. The separations are not very large (200 to 2,000  $\text{cm}^{-1}$ ); hence there is a large temperature-independent term in the susceptibility, the spin-lattice relaxation time is strongly temperature dependent ( $\propto T^{-7}$ ) in the liquid-helium region, and paramagnetic resonance can be observed only below 20 K. Then only the lowest doublet is occupied, effective  $S = \frac{1}{2}$ ,  $g$  is quite anisotropic (with accurately tetragonal symmetry; see Bleaney et al. [46]).  $g_{\parallel} = 6.45$ ;  $g_{\perp} = 3.05$  [47]. The  $z$  axes of the two ions in the unit cell are inclined to each other at an angle  $2\alpha$ , where  $\alpha = 34 \text{ deg}$ . The susceptibility can be calculated from  $\chi_{\parallel} - \chi_{\perp} = \cos^2 \alpha + \chi_{\perp} \sin^2 \alpha$ , for the  $K_1$  axis.  $\text{Co}^{59}$ ,  $I = \frac{7}{2}$ , is 100 percent abundant, and the nuclear contribution to the specific heat,  $b_n$ , is given [26] by  $\frac{2}{15} \frac{1}{8} (A_x^2 + A_y^2 + A_z^2)$ , with the  $A$ 's in kelvins. From  $A_z = 0.0245$ ,  $A_x = A_y = 0.002 \text{ cm}^{-1}$ , one finds that  $b_n = 1.66 \times 10^{-3} \text{ K}^2$ , which is to be compared with the experimental values [35,48,49] of 1.6 to  $1.8 \times 10^{-3}$ . The total specific heat  $b \approx 4.2 \times 10^{-3}$ , and  $b_i$  (calculated)  $= 2.1 \times 10^{-3}$ .

Adiabatic demagnetization experiments have been carried out by Garrett [50] and Miedema et al. [45];  $T_c = 0.084 \text{ K}$ ;  $S_c/R = 0.43$ .

9. *Cobaltous Fluosilicate*.  $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$ ; gram-ionic weight, 309.10; density, 2.113;  $\text{Co}^{2+}$ ;  $3d^7$ ;  ${}^4F_{3/2}$ .

The discussion is the same as for cobaltous ammonium sulfate, except that there is only one ion in the unit cell. The "parallel" and "perpendicular" axes of the magnetic complex coincide with those of the crystal and with the susceptibility axes.  $g_{\parallel} = 5.82$ ;  $g_{\perp} = 3.44$ ;  $A = 0.0184$ ,  $B = 0.0047 \text{ cm}^{-1}$  [47]. Benzie, Cooke, and Whitley [35]

find that  $b$  is large ( $18.5 \times 10^{-3} \text{ K}^2$ ) and almost entirely due to exchange interaction. Isotropic exchange would give rise to a Curie-Weiss constant of 0.23 K, but none was detected. Van den Broek, van der Marel, and Gorter [49], however, obtained  $bR/c_{\parallel} = 0.45 \times 10^6$  and  $bR/c_{\perp} = 1.74 \times 10^6$ , values which would require the principal  $g$ -values to be 6.04 and 3.07 in order to yield the above mentioned figure for  $b$ .

10. *Nickel Fluosilicate*.  $\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$ ; gram-ionic weight, 308.85; density, 2.134;  $\text{Ni}^{2+}$ ;  $3d^8$ ;  ${}^3F_4$ .

A cubic field leaves an orbital singlet lowest, and this spin triplet is split by a trigonal or tetragonal field into a doublet and a singlet and by a rhombic field into three singlets. Penrose and Stevens [51] found that  $g = 2.29$  and is isotropic; the doublet lies lowest ( $D$  negative) and  $D$  is constant at  $0.12 \text{ cm}^{-1}$  below 20 K but increases to  $0.17 \text{ cm}^{-1}$  at 90 K and  $0.32 \text{ cm}^{-1}$  at 195 K. Nickel in zinc fluosilicate behaves similarly [52] except that at all temperatures from 20 to 300 K the splitting is about 20 percent greater in the dilute (1:4 and 1:16) salts.

$b = 0.013 \text{ K}^2$  [35]; the contribution from the Stark splitting ( $-2D^2/9$ ) is  $6.0 \times 10^{-3}$  taking  $D = 0.173 \text{ K}$  and from magnetic dipole interaction is  $2 \times 10^{-3}$ . For a 1:16 zinc-diluted specimen,  $b = 0.012 \text{ K}^2$ . Investigations were carried out down to 0.02 K with a 15:85 Ni-Zn specimen by Hill, Meyer, and Milner [53]. They found that this salt obeyed the Curie law in the region of 1 K, and since the susceptibility is given by

$$\chi = \frac{C}{T} \left( 1 - \frac{D}{3kT} + \frac{\theta}{T} \right)$$

then the Weiss constant  $\theta \approx D/3k$ , or about 0.07 K, taking  $D = -0.14 \text{ cm}^{-1}$ . Thus the exchange is antiferromagnetic, in contrast to the experience of Benzie and Cooke [27] with the concentrated salt, where  $\theta' = +0.1 \text{ K}$ , i.e.,  $\theta = +0.04 \text{ K}$ , using  $D = -0.12 \text{ cm}^{-1}$ . From epr linewidth studies below 1 K, Svare and Seidel [54] showed that the exchange with the six nearest neighbor ions is ferromagnetic and isotropic, with the exchange constant  $= -3.9 \times 10^{-18} \text{ erg}$ . These authors give  $g = 2.24$  and  $D = -0.113 \text{ cm}^{-1}$ .

Extensive magnetothermodynamic investigations have been carried out by Giaque et al. [55] and used to derive absolute temperatures in the range 0.05 to 0.3 K.

11. *Cupric Potassium Sulfate*.  $\text{CuSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ ; gram-ionic weight, 441.97; density, 2.22;  $\text{Cu}^{2+}$ ;  $3d^9$ ;  ${}^2D_{3/2}$ .

This is a Tutton salt. The orbital levels are split by a cubic field into an upper triplet and a lower doublet. In a tetragonal or rhombic field, the doublet is further split into two singlets separated by about  $10^4 \text{ cm}^{-1}$ . These are twofold degenerate in spin, and hence at low temperatures effectively  $S = \frac{1}{2}$ .

The symmetry is rhombic [46]: For a zinc-diluted specimen  $g_z, g_x, g_y = 2.42, 2.16$ , and 2.04, respectively;  $A_z, A_x, A_y = -99, <17$ , and  $+61 \times 10^{-4} \text{ cm}^{-1}$ , respectively (these are the mean values for the two isotopes  $\text{Cu}^{63}$  and  $\text{Cu}^{65}$ , weighted in proportion to their natural abundances, viz., 69.1 and 30.9 percent, respectively). The  $z$  axes of the two ions in the unit cell are inclined to each other at an angle  $2\alpha$ , where  $\alpha = 43 \text{ K}$ . The theoretical value of  $b_n = \frac{5}{18}(A_x^2 + A_y^2 + A_z^2) = 0.97 \times 10^{-4} \text{ K}^2$ . Experimentally,  $b = 5.7 \times 10^{-4}$ ,  $b_n = 1.0 \times 10^{-4} \text{ K}^2$ . The interaction contribution is thus  $4.7 \times 10^{-4}$ , of which dipole-dipole coupling accounts for  $1.3 \times 10^{-4}$  [35]. The nuclear hfs entropy  $= R \ln 4$  or  $1.386R$ . Bleaney, Penrose, and Plumpton [56] observed that the epr lines of the undiluted salt showed "exchange narrowing." Their spectrum parameters, obtained at 90 K, differed from those cited above for the diluted salt in that  $g_z = 2.36$ ,  $g_x = 2.14$ , and  $\alpha = 42 \text{ deg}$ .

The magnetic cooling field is clouded by early entropy calculations being made using incorrect  $g$  values and by the questionable practice—for anisotropic substances—of working with powder specimens.  $T_c \approx 0.05 \text{ K}$  [57].



12. *Cupric Sulfate*.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ; gram-ionic weight, 249.69; density, 2.279;  $\text{Cu}^{2+}$ ;  $3d^9$ ;  ${}^2D_{3/2}$ .

The discussion is the same as for cupric potassium sulfate, except that the exchange energy between neighboring magnetic complexes is rather large ( $\sim 0.15 \text{ cm}^{-1}$ ) and of the order of magnitude of a microwave quantum; hence the details of an epr spectrum will depend upon the microwave frequency used.

There are two ions in the unit cell.  $g_{\parallel} = 2.47$  and  $g_{\perp} = 2.06$  [58]. The angle between the tetragonal axes is approximately 90 deg, and, as a result,  $\chi$  has an axis of symmetry normal to the plane of these two axes. The susceptibility along this symmetry axis  $\chi_a$  is equal to  $\chi_{\perp}$ , while in any direction in the plane of the tetragonal axes the susceptibility  $\chi_e$  has the value  $\frac{1}{2}(\chi_{\parallel} + \chi_{\perp})$  [59]. The exchange interaction gives rise to a Weiss constant of  $-0.6 \text{ K}$  [60]. The Curie constants per mole are  $C_a = 0.407$  and  $C_e = 0.480$ . Benzie and Cooke [60] combined their results with a reinterpretation of the measurements of Krishnan and Mookherji [59] to show that the susceptibility contains a temperature-independent term, with anisotropy ( $\chi_e - \chi_a$ ) of magnitude  $65 \times 10^{-6}$  per mole. This is in excellent agreement with the theoretical predictions of Polder [61]; viz.,

$$\chi_a = \frac{0.40}{T} + 20 \times 10^{-6} \quad \chi_e = \frac{0.48}{T} + 78 \times 10^{-6}$$

The specific heat shows a rounded maximum at 1.4 K and a  $\lambda$ -type anomaly at 0.034 K [62]. Studies by Geballe and Giauque [63] led those authors to suggest that the two inequivalent  $\text{Cu}^{++}$  ions in the unit cell give rise to two systems of ions with different environments, and hence differing low-temperature behavior. This picture was supported by specific heat and susceptibility determinations by Miedema et al. [64] who found that below 1 K the Curie constant fell to one-half its high-temperature value and  $\theta'$  changed to about  $+0.02 \text{ K}$ . More detailed information on the interactions were furnished in proton magnetic resonance studies by Wittekoek, Poullis, and Miedema [65]. Extensive magnetothermodynamic measurements by Giauque et al. [62] enabled them to derive absolute temperatures in the range 0.02 to 0.4 K.

13. *Cerous Magnesium Nitrate*.  $2\text{Ce}(\text{NO}_3)_3 \cdot 3\text{Mg}(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$ ; gram-ionic weight, 764.85; density, 2.10;  $\text{Ce}^{3+}$ ;  $4f^1$ ;  ${}^2F_{3/2}$ .

The  $J = \frac{7}{2}$  state lies about  $2,500 \text{ cm}^{-1}$  above the ground state. Under the combined action of the spin-orbit coupling and the electrostatic field (of  $C_{3v}$  symmetry) the  $J = \frac{5}{2}$  multiplet is split into three doublets. For simplicity these may be referred to as the  $J_z = \pm \frac{1}{2}$ ,  $\pm \frac{3}{2}$ , and  $\pm \frac{5}{2}$  levels, although actually the  $|\pm \frac{1}{2}\rangle$  and  $|\pm \frac{5}{2}\rangle$  states are mixed and there are, furthermore, small admixtures from the  $J = \frac{7}{2}$  manifold [66]. The salt is very anisotropic with  $g_{\parallel} \leq 0.026$  [67] and  $g_{\perp} = 1.840$  [68]. There is one magnetic ion in the unit cell.

The  $J_z = \pm \frac{3}{2}$  level lies at  $25.2 \text{ cm}^{-1}$  [69] and causes the spin-lattice relaxation time to vary exponentially with  $T$  in the region of 2 K [70]. There is a relatively large temperature-independent term in the susceptibility (0.002 cgs/mole) [71]. Measurements of  $\chi$  between 1.5 and 36 K [72] indicate that the third doublet lies at about 100 K.

The low-temperature specific heat is extremely small and is entirely accounted for by magnetic dipole interaction [73] plus the (in this instance not entirely negligible) lattice contribution; the Debye  $\theta$  is  $\sim 60 \text{ K}$  [74];  $b = 6 \times 10^{-6} \text{ K}^2$ . The salt obeys Curie's law down to below 0.01 K [73], and hence is much used in magnetic cooling applications. Its extreme anisotropy and Curie law behavior have been made use of by Cooke, Meyer, and Wolf [31] to determine the  $\chi$ - $T$  relation for several isotropic substances (by a compound-specimen technique) down to 0.05 K. Absolute temperature determinations down to the region of 0.001 K by different methods [75,76] are in reasonably close agreement. Marked deviations from Curie's law set in below 6 mK,

despite the fact that  $\theta'$  is only  $-0.27$  mK [77]. Wheatley [78] has obtained evidence that agglomerations of powdered CMN obey Curie's law down to as low as 2 mK.

14. *Cerous Ethyl Sulfate*.  $\text{Ce}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ ; gram-ionic weight, 677.66; density, 1.839;  $\text{Ce}^{3+}$ ;  $4f^1$ ;  ${}^2F_{3/2}$ .

The discussion is the same as for cerous magnesium nitrate, except that the crystal field has  $C_{3h}$  symmetry [79] and there are two ions in the unit cell although with a unique magnetic axis. The  $J_z = +\frac{5}{2}$  level lies lowest, and the  $J_z = \pm\frac{1}{2}$  level is at 0.6 K higher. In a crystal diluted 200:1 with lanthanum ethyl sulfate this order of levels was found to be inverted [80]. The third doublet ( $J_z = \pm\frac{3}{2}$ ) is at some 200  $\text{cm}^{-1}$  above the ground state. ( $J_z$  is not truly a good quantum number; compare cerous magnesium nitrate.) For the  $\pm\frac{5}{2}$  level,  $g_{\parallel} = 3.80$ ,  $g_{\perp} = 0.22$ ; for the  $\pm\frac{1}{2}$  level,  $g_{\parallel} = 1.0$ ,  $g_{\perp} = 2.2$  [81].

Between 0.3 and 1 K, the specific heat is given by [81]

$$\frac{cT^2}{R} = b_i + \delta^2 \exp\left(-\frac{\delta}{T}\right) \left[1 + \exp\left(-\frac{\delta}{T}\right)\right]^{-2}$$

with  $\delta = 6.6$  K. The magnitude of  $b_i$ ,  $11.2 \times 10^{-4}$ , is six times that to be expected from magnetic dipole interaction [82] and is thought to arise mainly from electric quadrupole-quadrupole interaction between the cerium ions [83,84]. Supporting evidence was obtained from epr measurements below 1 K by Baker [85]. There is a temperature-independent term in  $\chi_{\perp}$  of magnitude  $4.7 \times 10^{-4}$  emu/mole [80]. In the liquid-helium region the susceptibility along the crystal axis is given by

$$\chi_{\parallel} = \frac{C}{T} (1 - A)$$

$$\text{where } C = \frac{N\mu_B^2}{4k} g_{\parallel} \left(\frac{5}{2}\right)^2 \quad A = \frac{g_{\parallel} \left(\frac{5}{2}\right)^2 - g_{\parallel} \left(\frac{1}{2}\right)^2}{g_{\parallel} \left(\frac{5}{2}\right)^2 [1 + \exp(\delta/T)]}$$

Adiabatic demagnetization studies have been carried out down to 0.02 K by Johnson and Meyer [84];  $T_c = 0.05$  K at  $S/R = 0.48$ . Meyer and Smith [86] have measured the specific heat between 0.6 and 20 K. They find that  $\delta = 6.7$  K and also observe an excess specific heat in the region of the maximum of the Schottky anomaly. This has been explained by Becker and Clover [87] in terms of an anomalous phonon spectrum arising from the spin-phonon interaction, taking account of the substantial broadening of the lowest energy levels.

15. *Neodymium Magnesium Nitrate*.  $2\text{Nd}(\text{NO}_3)_3 \cdot 3\text{Mg}(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$ ; gram-ionic weight, 768.99; density, ;  $\text{Nd}^{3+}$ ;  $4f^3$ ;  ${}^4I_{3/2}$ .

The  ${}^4I_{3/2}$  ground state is split by a crystalline electric field of  $C_{3v}$  symmetry [66] into five Kramers doublets. At liquid-helium temperatures only the lowest of these is populated. This is a mixture of states with  $J_z = \pm\frac{7}{2}$ ,  $\pm\frac{1}{2}$ ,  $\pm\frac{5}{2}$ .  $g_{\parallel} = 0.45$ ;  $g_{\perp} = 2.72$  [87]. The low-temperature thermal and magnetic behavior is modified by nuclear hyperfine coupling.  $\text{Nd}^{143}$  (12.20 percent) and  $\text{Nd}^{145}$  (8.30 percent) both have  $I = \frac{7}{2}$ , resulting in a contribution to the entropy of  $0.205R \ln 8$  or  $0.426R$ . The hfs parameters in the spin Hamiltonian are:  $B_{143} = 0.0312$ ,  $B_{145} = 0.0194$ ,  $A_{143} \sim 0.005$ ,  $A_{145} \sim 0.003 \text{ cm}^{-1}$ .

Adiabatic demagnetization experiments down to 0.06 K have been made by Cooke, Meyer, and Wolf [31,34]. Deviations from Curie's law begin at 0.1 K, owing to the influence of the hfs.  $b = 8.74 \times 10^{-4} \text{ K}^2$ . Calculated values are:  $b_i = 3.0 \times 10^{-5}$ ,  $b_{143} = 6.53 \times 10^{-4}$ ,  $b_{145} = 1.70 \times 10^{-4} \text{ K}^2$ . Spin-lattice relaxation in the liquid-helium region has been investigated by Hudson and Mangum [88] and down to 0.3 K, in lanthanum-diluted crystals, by Jeffries et al. [89]. The Zeeman effect in the

optical spectrum has been studied in detail by Dieke and Heroux [90]. Their values for  $g_{\parallel}$  and  $g_{\perp}$  for the ground state (0.420 and 2.629, respectively) are in reasonably good agreement with the epr data. They obtain 3.38 and zero for the  $g$  values of the  $J_z = \pm \frac{3}{2}$  level, which is found to lie at  $33.13 \text{ cm}^{-1}$ .

16. *Neodymium Ethylsulfate*.  $\text{Nd}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ ; gram-ionic weight, 681.80; density, 1.872;  $\text{Nd}^{3+}$ ;  $4f^3$ ;  $^4I_3$ .

The  $^4I$  ground state lies about  $1,800 \text{ cm}^{-1}$  below the next higher level. In a crystal field of  $C_{2h}$  symmetry it is split into five doublets and only the lowest is effectively occupied at 20 K and below. This is a mixture of the basic  $J_z$  states  $|\pm \frac{3}{2}\rangle$  and  $|\pm \frac{5}{2}\rangle$  [79c]. The first excited doublet,  $|+\frac{1}{2}\rangle$ , lies at  $150 \text{ cm}^{-1}$  (see below). There is one ion in the unit cell.

Detailed paramagnetic resonance investigations have been made by Bleaney, Scovil, and Trenam [91], who find discrepancies between the strong field and weak field results. The Hamiltonian of Eq. (5f-1) cannot be fitted to the latter. A possible explanation is that given by Stevens to account for the similar but much larger effects in gadolinium ethyl sulfate: viz., here one is not dealing with a static crystalline electric field, but the equilibrium positions of the surrounding dipoles may depend upon the state of the magnetic ion.  $g_{\parallel} = 3.535$ ;  $g_{\perp} = 2.072$ . The hfs parameters in the spin Hamiltonian are:  $A_{143} = 0.0380$ ,  $A_{145} = 0.0236$ ,  $B_{143} = 0.0199$ ,  $B_{145} = 0.0124 \text{ cm}^{-1}$ . (See also Erickson [92]).

Optical transitions and the Zeeman effect have been studied by Dieke and Heroux [90], who obtain  $g_{\parallel} = 3.50$  and  $g_{\perp} = 2.06$  for the lowest doublet. The next doublet lies at  $149.64 \text{ cm}^{-1}$ .

Low-temperature studies, between 0.015 and 2 K, were made by Meyer [93] ( $b = 1.13 \times 10^{-3} \text{ K}^2$ ), and in the liquid-helium region by Roberts, Sartain, and Borie [94] ( $b = 1.09 \times 10^{-3}$ ). The theoretical value for  $b_e$  is  $0.176 \times 10^{-3} \text{ K}^2$ , and from the epr data one calculates  $b_{143} = 6.073 \times 10^{-3}$ ,  $b_{145} = 2.348 \times 10^{-3} \text{ K}^2$ ; these together lead to a theoretical value of  $1.11 \times 10^{-3} \text{ K}^2$  for  $b$ .  $T_c \approx 0.016 \text{ K}$  at  $S/R \sim 0.45$ . The theory of dipole-dipole interaction in anisotropic crystals and of the added effect on  $\chi$  of the hfs developed by Daniels [82] has been applied to this salt by Meyer. The effect is much larger for the "parallel" direction ( $2\frac{1}{2}$  percent correction at 0.5 K) than for the "perpendicular" direction (2 percent correction at 0.2 K). Blok, Shirley, and Stone [95] have determined the susceptibility temperature scale down to 0.01 K, using both gamma-ray heating and nuclear orientation methods. Their values of  $T$  agree with those of Meyer [93] down to 0.025 K. The specific heat between 1.5 and 20 K has been measured by Meyer and Smith [86]. The lattice contribution  $c_l$  showed the same features here as in several rare-earth ethyl sulfates; viz.,  $c_l/T^3$  fell rapidly between 1.5 and 3 K, then rose again, and passed through a broad maximum at 8 to 9 K, falling slowly with further increase of temperature.

17. *Gadolinium Sulfate*.  $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ ; gram-ionic weight, 373.42; density, 3.010;  $\text{Gd}^{3+}$ ;  $4f^7$ ;  $^8S$ .

The free ion having an  $^8S$  ground state, the effect of the crystalline electric field is small and the splittings produced are only of the order of  $1 \text{ cm}^{-1}$ . Hebb and Purcell [96] showed that the eightfold degenerate ground level is split by a cubic field into two doublets and a quadruplet, and specific-heat data have always been interpreted on this basis. Epr studies at room temperature by Bogle and Heine [97] on a 200:1 samarium-diluted crystal showed, however, that there are four doublets lying at 0, 0.20, 0.48, and  $0.82 \text{ cm}^{-1}$ , respectively. There are two magnetically inequivalent ions in the unit cell, the crystal  $b$  axis being the twofold axis.  $g = 1.99$  and is isotropic.

The spin Hamiltonian can be written most conveniently

$$\mathcal{H} = g\mu_B\mathcal{B} \cdot \mathbf{S} + B_2^0 P_2^0 + B_2^2 P_2^2 + B_4^0 P_4^0$$

TABLE 5f-35. PROPERTIES OF PARAMAGNETIC SALTS

Paramagnetic salt	Gram-ionic weight $M$ , g	Room-temp. density $\rho$ , g/cm <sup>3</sup>	$g$ values	Curie const. $C$ , emu/g-ion	$D$ , cm <sup>-1</sup>	Spec. heat const $b$ , K <sup>2</sup>
1. Titanium cesium alum TiCs(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O	589	2.019	$g_{\parallel} = 1.25$ $g_{\perp} = 1.14$	0.130 <sup>a</sup>	.....	$3.9 \times 10^{-5}$
2. Chromic potassium alum CrK(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O	499	1.83	1.98	1.84	0.135 0.075 <sup>b</sup>	$1.8 \times 10^{-2}$
3. Chromic methylammonium alum Cr(CH <sub>3</sub> NH <sub>2</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O	492	1.645	1.976	1.83	0.087	$1.9 \times 10^{-2}$
4. Vanadous ammonium sulfate V(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	387	.....	1.95	1.78	0.15 <sub>3</sub> <sup>d</sup>	$5.6 \times 10^{-2}$
5. Ferric ammonium alum Fe(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O	482	1.71	2.003	4.39	0.016 <sup>f</sup>	$\sim 1.3 \times 10^{-2}$
6. Ferric methylammonium alum Fe(CH <sub>3</sub> NH <sub>2</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O	490	1.659	2.003	4.39	0.188 <sup>g</sup>	0.45
7. Manganous ammonium sulfate Mn(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	391	1.83	2.00	4.38	0.027 <sup>h</sup>	$3.2 \times 10^{-2}$
8. Cobaltous ammonium sulfate Co(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	395	1.902	$g_{\parallel} = 6.45$ $g_{\perp} = 3.05$	2.95 <sup>i</sup>	..... <sup>j</sup>	$4.2 \times 10^{-2}$
9. Cobaltous fluosulfate CoSiF <sub>6</sub> ·6H <sub>2</sub> O	309	2.113	$g_{\parallel} = 5.82$ $g_{\perp} = 3.44$	$C_{\parallel} = 3.18$ $C_{\perp} = 1.11$	..... <sup>k</sup>	$(18.5 \times 10^{-2})^l$
10. Nickel fluosulfate NiSiF <sub>6</sub> ·6H <sub>2</sub> O	309	2.134	2.29	1.31 <sup>m</sup>	-0.12 <sup>n</sup>	$1.3 \times 10^{-2}$
11. Cupric potassium sulfate CuK <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	442	2.22	$g_x = 2.14$ $g_y = 2.04^o$ $g_z = 2.36$ .....	0.445 <sup>p</sup>	.....	$5.7 \times 10^{-1}$
12. Cupric sulfate CuSO <sub>4</sub> ·5H <sub>2</sub> O	250	2.281	.....	$C_{\parallel} = 0.480$ $C_{\perp} = 0.407^q$	.....	.....

13. Cerous magnesium nitrate $Ce_2Mg_3(NO_3)_{12} \cdot 24H_2O$	765	2.10	$g_{\parallel} \leq 0.026$ $g_{\perp} = 1.840$	$C_{\perp} = 0.317$	.....	$6 \times 10^{-6}$
14. Cerous ethylsulfate $Ce(C_2H_5SO_4)_3 \cdot 9H_2O$	678	1.839	$g_{\parallel} = 3.80$ $g_{\perp} = 0.22^c$	$C_{\parallel} = 1.35$ $C_{\perp} = 0.0045$	.....	$1.12 \times 10^{-3}$
15. Neodymium magnesium nitrate $Md_2Mg_2(NO_3)_{12} \cdot 24H_2O$	769	2	$g_{\parallel} = 0.45$ $g_{\perp} = 2.72$	$C_{\parallel} = 0.019$ $C_{\perp} = 0.694$	.....	$8.74 \times 10^{-45}$
16. Neodymium ethyl sulfate $Nd(C_2H_5SO_4)_3 \cdot 9H_2O$	682	1.872	$g_{\parallel} = 3.535$ $g_{\perp} = 2.072$	$C_{\parallel} = 1.170$ $C_{\perp} = 0.402$	.....	$11.1 \times 10^{-16}$
17. Gadolinium sulfate $Gd_2(SO_4)_3 \cdot 8H_2O$	373	3.0-0	1.99	7.80	0.0633 <sup>a</sup>	0.32 or 0.37 <sup>b</sup>

<sup>a</sup>  $1/2 g_{\parallel} + 1/2 x_{\perp}$ .

<sup>b</sup> Two types of ion below 160 K.

<sup>c</sup>  $1.7 \times 10^{-2}$  using epr data.

<sup>d</sup>  $E = 0.04_0$  cm<sup>-1</sup>.

<sup>e</sup>  $b_2/E$ , Stark contribution (calculated from epr data).

<sup>f</sup>  $a = -0.0128$  cm<sup>-1</sup>; splitting sensitive to temperature and dilution.

<sup>g</sup>  $a = 0.010$  cm<sup>-1</sup>; splitting little affected by dilution.

<sup>h</sup>  $E = 0.005$ ,  $a = 0.0008$ ,  $A = 0.0093$  cm<sup>-1</sup>;  $D$  and  $E$  sensitive to temperature and dilution.

<sup>i</sup> Along  $K_1$  axis.

<sup>j</sup>  $A = 0.0245$ ,  $B = 0.002$  cm<sup>-1</sup>. Tetragonal axes 68 deg apart.

<sup>k</sup>  $A = 0.0184$ ,  $B = 0.0047$  cm<sup>-1</sup>.

<sup>l</sup> Conflicting experimental data.

<sup>m</sup> Weiss  $\theta \sim -0.07$  K.

<sup>n</sup>  $D$  varies with temperature and dilution.

<sup>o</sup> Rhombic symmetry;  $z$  axes 84 deg apart.

<sup>p</sup> For powder. Weiss  $\theta \sim 0.035$  K.

<sup>q</sup> Tetragonal axes  $\sim 90$  deg apart. Weiss  $\theta \sim -0.6$  K.

<sup>r</sup> Second doublet at 4.6 cm<sup>-1</sup> with  $g_{\parallel} = 1.0$ ,  $g_{\perp} = 2.2$ ; order of levels inverted in diluted salt.

<sup>s</sup> Mostly due to hfs.

<sup>t</sup> Mostly due to hfs.

<sup>u</sup>  $E = 0.013$ ,  $F = 0.004$  cm<sup>-1</sup>. Spectrum observed at room temperature.

<sup>v</sup> All experiments give one of the other of these two figures.

where the  $P_n^m$  are operators [26,79c] which have the same transformation properties as the corresponding spherical harmonics  $Y_n^m$ , and  $B_n^m$  are coefficients determined by fitting to the observed spectrum. The findings are:  $b_2^0 = 3B_2^0 = 0.0633$ ,  $b_2^2 = 3B_2^2 = 0.038$ ,  $b_4^0 = 60B_4^0 = -0.0013 \text{ cm}^{-1}$ . The Stark specific-heat term  $b_e$  is calculated to be  $0.195 \text{ K}^2$  from the expression  $21(b_2^0)^2 + 7(b_2^2)^2 + 77(b_4^0)^2$ , in kelvins, while  $b_i = 0.10 \text{ K}^2$ ; adding, one finds that  $b = 0.30 \text{ K}^2$ . The last figure is notably smaller than that which is obtained from relaxation experiments [98] between 77 and 290 K. These give  $bR/C = 3.0 \times 10^6 \text{ Oe}^2$ , and taking  $C/R = 9.38 \times 10^{-8} \text{ K}^2 \text{ Oe}^{-2}$ ,  $b = 0.37 \text{ K}^2$ . There are discrepancies among different measured values at low temperatures, viz., 0.32 from relaxation experiments [99-101], 0.37 from adiabatic demagnetization [102] and calorimetry [103]. The  $T^{-2}$  dependence of the specific heat breaks down below 3 K, owing to the large value of  $D (= b_2^0)$ , and relaxation-type determinations involve rather large corrections for saturation effects owing to the large Curie constant.

Giauque and MacDougall [104] used this substance for their pioneering magnetic cooling experiments in 1933. Because of its large specific heat it is most useful as a cooling substance in the 0.1 to 1 K range (compare ferric methylammonium alum). Van Dijk [105] has measured the departures from the Curie Law down to 0.22 K.

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**5f-16. Susceptibility in High Magnetic Fields.**<sup>1</sup> The magnetic behavior of materials in high magnetic fields ( $H \gtrsim 25$  kOe) can yield useful information whether the material is paramagnetic (P), ferromagnetic (F), ferrimagnetic ( $F_i$ ), antiferromagnetic (A), weakly ferromagnetic (WF), i.e., canted antiferromagnetism, or some combination of these. In Table 5f-36, an abbreviated notation is used to give a capsule view of the type of behavior encountered.

For usual paramagnetics, a comparison with a Brillouin curve reflecting the energy-level structure and the paramagnetic saturation moment (PS) are of interest. Special cases occur with ions whose ground state is nonmagnetic and whose magnetization is induced rather than aligned. Closely related behavior also occurs as a residual high-field susceptibility ( $\chi_{HF}$ ) of the Van Vleck type ( $\chi_{VV}$ ) after saturation by alignment. Other phenomena embraced by residual  $\chi_{HF}$  are electron band susceptibility (band), magnetic sublattice rotation or a less well organized aligning process against antiferromagnetic interactions, magnetization rotation in monocrystals against large anisotropies ( $K$ ), approach to ferro- or ferrimagnetic saturation (FS) in polycrystalline samples, and puzzling jumps in  $\chi$  vs.  $H$  above the antiferromagnetic Néel point ( $d\chi/dH$ ;  $T > T_N$ ).

A large number of substances undergo first-order transitions as a function of temperature at  $H = 0$  between two different ordered magnetic states below the paramagnetic region, e.g., A-F, A- $F_i$ , A-WF, etc. A related case is the first-order change from paramagnetic (P) to an ordered state. In all these instances a high field can induce a transition from the less magnetic state to the more magnetic one, as manifested by the externally measurable total magnetic moment. The critical fields for these transitions are distinctly temperature-dependent; i.e.,  $H_c(T - T_i)$ , where  $T_i$  is the transition temperature in vanishingly small field. These transitions lend themselves to thermodynamic analysis using the Clausius-Clapeyron equation. One should also note the spiral or helical antiferromagnetic or ferromagnetic-like states ( $A_h, F_h$ ) and their field-induced variants such as fan (Fan) or other intermediate states

<sup>1</sup> Prepared by I. S. Jacobs, General Electric Research and Development Laboratories.



TABLE 5f-36. MAGNETIZATION BEHAVIOR IN HIGH FIELDS

Substance	Behavior	$H_c$ , kOe, or $\chi_v$ , emu/cc	$T$ , K	Ref.
CeBi	A $\rightarrow$ F <sub>1</sub> $\rightarrow$ P	11, 43	1.3	1
CeSb	A $\rightarrow$ F <sub>1</sub> <sup>I</sup> $\rightarrow$ F <sub>1</sub> <sup>II</sup> $\rightarrow$ P	7, 22, 38 $H \parallel [100]$	1.5	2
CoBr <sub>2</sub> ·2H <sub>2</sub> O	A $\rightarrow$ F <sub>1</sub> $\rightarrow$ P	13.7, 29.8 $H \parallel b$	4.2	3
CoCl <sub>2</sub>	SF $\rightarrow$ P, $dx/dH$	34 $H \perp c$	4.2	4
CoCl <sub>2</sub> ·9H <sub>2</sub> O	A $\rightarrow$ F <sub>1</sub> $\rightarrow$ P	31.6, 46.0 $H \parallel b$	4.2	3, 5
CoF <sub>2</sub>	A $\rightarrow$ WF	130 $H \perp c$	4.2	6, 7
$\beta$ -Co(OH) <sub>2</sub>	SF $\rightarrow$ P, $dx/dH$	35 $H \perp c$	4.2	8
$\beta$ -CoSO <sub>4</sub>	A $\rightarrow$ WF	12.5 $H \parallel c$	4.2	9
Co <sub>2</sub> Y	K	$K = 5.7 \times 10^7$ erg/cc	300	10
CoUO <sub>4</sub>	A $\rightarrow$ P	55	4.2	11
Cr	$dx/dH$	$\Delta\chi/\chi < 0$ , $\approx 300$ kOe	295	12
Cr <sub>2</sub> BeO <sub>4</sub>	A <sub>1</sub> $\rightarrow$ Fan (?)	30, $H \parallel b$ ; 48, $H \parallel c$	4.2	13
Cr <sub>2</sub> CuO <sub>4</sub>	XHF	$1.3 \times 10^{-4}$	4.2	14
Cr <sub>2</sub> FeO <sub>4</sub>	XHF	$3.9 \times 10^{-4}$	4.2	14
CrK(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O	PS	$3.0\mu_B/\text{Cr}^{3+}$	1.3	15
Cr <sub>2</sub> MnO <sub>4</sub>	XHF	$3.6 \times 10^{-4}$	4.2	14
CrNaS <sub>2</sub>	A $\rightarrow$ SF $\rightarrow$ P	20, 138 $H \perp c$	$\sim 4$	16, 17
Cr <sub>2</sub> O <sub>3</sub>	A $\rightarrow$ SF	50 $H \parallel c$	4.2	18
Cr <sub>2</sub> ZnSe <sub>4</sub>	A <sub>1</sub> $\rightarrow$ P	64	4.2	19
Cu <sub>0.5</sub> Cd <sub>0.2</sub> Fe <sub>2</sub> O <sub>4</sub>	XHF	$7 \times 10^{-4}$ , $> 110$ kOe	300	20
CuCl <sub>2</sub> ·2H <sub>2</sub> O	A $\rightarrow$ SF $\rightarrow$ P, $dx/dH$	7, 150	1	21
Cu(NO <sub>3</sub> ) <sub>2</sub> ·2.5H <sub>2</sub> O	A $\rightarrow$ P	35 $H \parallel b$	1.2	22
Dy	K	$K = 4.9 \times 10^8$ erg/cc	4.2	23
Dy <sub>3</sub> Al <sub>2</sub>	A(?) $\rightarrow$ F, $H_c(T - T_i)$	21, $T_i = 20^\circ$	4.2	23a
DyAu	A $\rightarrow$ P	22	4.2	24
DyCu <sub>2</sub>	A <sub>1</sub> $\rightarrow$ P	$\approx 20$	4.2	25
DyEr <sub>3</sub>	A <sub>1</sub> $\rightarrow$ X $\rightarrow$ F	22, 45 $H \parallel a$	4.2	26
DySb	A $\rightarrow$ F <sub>1</sub> $\rightarrow$ P	22, 40 $H \parallel [100]$	1.5	27
Er	F <sub>1</sub> $\rightarrow$ X $\rightarrow$ F	20, 140 $H \perp c$	4.2	26
ErSb	A $\rightarrow$ P, $dx/dH$	25	1.5	27
EuTe	SF $\rightarrow$ P, $dx/dH$	75	2.1	4, 28
Fe	XHF, Band	$3.2 \times 10^{-5}$ , $4.3 \times 10^{-5}$	4.2	29-31
Fe <sub>0.5</sub> Al <sub>0.17</sub>	XHF, Band	$3.0 \times 10^{-5}$	4.2	32
FeBr <sub>2</sub>	A $\rightarrow$ P; XFF	31.5 $H \parallel c$	2	33
FeCO <sub>3</sub>	A $\rightarrow$ P	$\sim 150$ $H \parallel c$	4.2	34, 6
FeCl <sub>2</sub>	A <sub>1</sub> $\perp$ $\rightarrow$ P, XHF	10.6, 100	4.2	35, 36
FeCl <sub>2</sub> ·2H <sub>2</sub> O	A $\rightarrow$ F <sub>1</sub> $\rightarrow$ P	39, 46 $H \parallel \alpha$	4.0	37
FeGe	A $\rightarrow$ SF	67	4.2	38
FeK <sub>3</sub> (CN) <sub>6</sub>	PS	$1.0\mu_B/\text{Fe}^{3+}$	1.3	39
FeNH <sub>4</sub> (SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O	PS	$5.0\mu_B/\text{Fe}^{3+}$	1.3	15, 39
Fe <sub>0.5</sub> Ni <sub>0.5</sub> Br <sub>2</sub>	A $\rightarrow$ X $\rightarrow$ P	35, 60 $H \perp c$	4.2	40
FeO	$dx/dH$ , $T \gtrsim T_N$	$H > 90$ , 150	150-400	41
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	A $\rightarrow$ SF	68 $H \parallel c$	77	42-44
	A <sub>1</sub> $\rightarrow$ WF	130, 162 $H \perp c$	120, 77	45, 46
FeRh	A $\rightarrow$ F, $H_c(T - T_i)$	270, 230; $T_i = 330^\circ$	77	47, 48
Fe <sub>7</sub> S <sub>8</sub>	K	$K \approx 10^7$ erg/cc	1.2-300	49
GdAlO <sub>3</sub>	A $\rightarrow$ SF $\rightarrow$ P, $dx/dH$	11, 34 $H \parallel b$	1	50, 51
GdAs	SF $\rightarrow$ P	165	1.6	52
GdCu <sub>2</sub>	A <sub>1</sub> $\rightarrow$ X $\rightarrow$ P	50, 100	4.2	53, 25
Gd <sub>2</sub> Fe <sub>3</sub> O <sub>12</sub>	XHF	$1 \times 10^{-3}$ , $H > 70$ kOe	300	54
GdP	SF $\rightarrow$ P	90	1.6	28
Gd <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·8H <sub>2</sub> O	PS	$7.0\mu_B/\text{Gd}^{3+}$	1.3	15
Ho	A $\rightarrow$ F (?)	106 $H \parallel c$	40	55, 23
HoAl	FS	$7.1 \pm 0.2\mu_B/\text{Ho}$	4.2	56
HoSb	A $\rightarrow$ F <sub>1</sub> $\rightarrow$ P	17, 23 $H \parallel [100]$	1.6	57
MnAs	P $\rightarrow$ F, $H_c(T, p)$	29( $p = 0$ ), 110( $p = 1$ kb)	307, 329	58
MnAus	A $\rightarrow$ SF	$\approx 47$	4.2	59, 60
MnCO <sub>3</sub>	$dx/dH$ , $T > T_N$	$\Delta\chi/\chi \approx 0.14$ , 150 kOe	300	61
MnCl <sub>2</sub>	A $\rightarrow$ SF $\rightarrow$ P, $dx/dH$	9, 32	1.3	62
MnCl <sub>2</sub> ·4H <sub>2</sub> O	A $\rightarrow$ SF $\rightarrow$ P; PS	7.5, 20.6 $H \parallel c'$	0.26; 1.3	63, 64
Mn <sub>1.5</sub> Cr <sub>0.5</sub> Sb	A $\rightarrow$ F <sub>1</sub> , $H_c(T - T_i)$	$\approx 100$ , $T_i = 305^\circ$	265	65
MnF <sub>2</sub>	A $\rightarrow$ SF	93 $H \parallel c$	4.2	66, 67
Mn <sub>1.21</sub> Fe <sub>0.69</sub> As	A $\rightarrow$ F, $H_c(T - T_i)$	64, $T_i = 283^\circ$	301	68
Mn <sub>2</sub> GaC	A $\rightarrow$ F, $H_c(T - T_i)$	150, $T_i = 150^\circ$	100	69
Mn <sub>2</sub> Ge <sub>2</sub>	A $\rightarrow$ WF, $H_c(T - T_i)$	190, $T_i = 160^\circ$	77	70, 65

TABLE 5f-36. MAGNETIZATION BEHAVIOR IN HIGH FIELDS (Continued)

Substance	Behavior	$H_c$ , kOe, or $\chi_v$ , emu/cc	T, K	Ref.
MnK <sub>2</sub> F <sub>4</sub> .....	A → SF	55 $H \parallel c$	4.2	71
Mn <sub>1-y</sub> LaO <sub>3</sub> .....	$\chi_{HF}$	$8 \times 10^{-4}$ , $0 \leq y \leq 0.05$	77	72
MnLiPO <sub>4</sub> .....	A → SF	40 $H \parallel a$	4.2	13
MnO.....	$\chi_{HF}$	$dx/dH > 0$ , $< 50$ kOe	4.2	73
MnO <sub>2</sub> .....	$dx/dH$ , $T > T_N$	$\Delta x/x \sim 0.6$ , $\sim 250$ kOe	300	61
		$\Delta x/x \approx 0$ , $< 300$ kOe	84, 4	74
Mn <sub>2</sub> O <sub>4</sub> .....	$\chi_{HF}$	$3.0 \times 10^{-4}$	4.2	75, 76
MnRb <sub>2</sub> F <sub>4</sub> .....	A → SF	51 $H \parallel c$	4.2	71
MnSO <sub>4</sub> .....	$\Lambda_h \rightarrow SF \rightarrow P$ , $dx/dH$	40, 250	1.6	77
	$dx/dH$ , $T > T_N$	$\Delta x/x \approx 0.19$ , 200 kOe	300	61
MnSO <sub>4</sub> ·H <sub>2</sub> O.....	A → SF → P, $dx/dH$	25, 320	1.6	77
	$dx/dH$ , $T > T_N$	$\Delta x/x \approx 0.12$ , $\approx 250$ kOe	300	61
MnSn <sub>2</sub> .....	A → WF, $H_c(T - T_i)$	120, $T_i = 73^\circ$	4.2	78
Ni.....	$\chi_{HF}$ , Band	$3 \times 10^{-5}$ , $1.7 \times 10^{-5}$	4.2	29-31
Ni <sub>2</sub> Al.....	$\chi_{HF}$ , Band	$9.8 \times 10^{-5}$ , 200 kOe	4.2	79
Ni <sub>2</sub> Ga.....	$\chi_{HF}$ , Band	$17 \times 10^{-5}$ , 200 kOe	4.2	79
Ni(OH) <sub>2</sub> .....	A → P	50 $H \parallel c$	4.2	80
Pd.....	$\chi_{HF}$ , Band	$8 \times 10^{-5}$	4.2, 0, 1	81, 82
R <sub>2</sub> Ga <sub>5</sub> O <sub>12</sub> .....	PS	.....	2.6	11
[R = Gd, Er, Yb]Sc <sub>3</sub> In.....	$\chi_{HF}$ , Band	$6.5 \times 10^{-5}$ , 40 kOe	1.2	83
Tb.....	K	$K = 4.5 \times 10^8$ erg/cc	4.2	23
Tb <sub>2</sub> Al <sub>2</sub> .....	$F_A(?) \rightarrow F$ , $H_c(T - T_i)$	30, $T_i = 10^\circ$	4	23a
TbAs.....	A → P	$\approx 30$	1.6	52
TbCu <sub>2</sub> .....	$\Lambda_h \rightarrow P$	22	4.2	25
Tm.....	F <sub>1</sub> → F	15, 28	4.2	84, 85
TmSb.....	Induced KHF	$M[100] < [110] < [111]$	1.6	86
Yb <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub> .....	$\chi_{HF}$	$1.4 \times 10^{-5}$	4.2	87
ZrZn <sub>2</sub> .....	$\chi_{HF}$ , Band	$7.3 \times 10^{-5}$	4.2	88

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(X). The notation (X) is also invoked when the nature of a state is not known, but its field region is well described.

Lastly, there is the particularly rich area for high-field studies in mapping out the magnetic phase diagrams of antiferromagnetics. As the field along the moment axis increases, there is often a transition from the antiferromagnetic state (A) to the transverse spin-flopped state (SF). This critical field is a measure of the anisotropy. For a further increase of the field, this state gives way to the nearly saturated P state. Sometimes this SF  $\rightarrow$  P behavior is nonlinear, i.e.,  $(d\chi/dH)_{H < H_c} = f(H)$ , arising from one or more higher-order interactions. In other cases, either in the presence of strong anisotropy or nearer to the Néel point, the transition A  $\rightarrow$  P is found, but with differing steepness during the transition, e.g., nearly first order, or distinctly second or higher order, respectively.

Workers in this rapidly expanded area are cautioned that pulsed field measurements tend to be isentropic rather than isothermal, which condition can seriously modify the results obtained.

**5f-17. Demagnetizing and Form Factors.**<sup>1</sup> The magnetic field strength  $\mathbf{H}$  in a magnetized body is given by

$$\mathbf{H} = \mathbf{H}_a + \mathbf{H}_D$$

where  $\mathbf{H}_a$  is the applied field due to outside sources and  $\mathbf{H}_D$ , called the demagnetizing field, is due to the effective magnetic poles in the body itself, which occur at points where the intensity of magnetization  $\mathbf{M}$  has nonvanishing divergence.

In a uniformly magnetized ellipsoid the effective poles are all on the surface, and they contribute a uniform demagnetizing field, with components along the principal axes,  $i = 1, 2$ , and 3, given by

$$(H_D)_i = -N_i M_i$$

where  $N_i$  is a constant, known as the demagnetizing factor for magnetization along  $i$ th principal axis. For any ellipsoid

$$N_1 + N_2 + N_3 = 4\pi$$

In terms of a set of axes not along the principal axes of the ellipsoid, the demagnetizing field is described by

$$(H_D)_k = - \sum_j N_{kj} M_j$$

<sup>1</sup> Prepared by W. J. Carr, Jr., Westinghouse Research and Development Center.

where the tensor components  $N_{kj}$  are easily calculated from the three demagnetizing factors.

In the general case of a nonellipsoidal body, or for nonuniform magnetization, the demagnetizing field varies from point to point, and the above description does not apply; however, many shapes can be approximated by some particular ellipsoid, and in this way if the magnetization is nearly uniform, approximate demagnetizing factors can be defined. For example, a rod is approximated by an elongated prolate ellipsoid of revolution, and a disk by a flattened oblate ellipsoid.

For ellipsoids of revolution, i.e., spheroids, in which the ratio of the long to the short axis is  $m$ , the demagnetizing factor  $N$  for magnetization along the long axis is as follows:

*Prolate Spheroid*

$$N = \frac{4\pi}{m^2 - 1} \left[ \frac{m}{\sqrt{m^2 - 1}} \log_e (m + \sqrt{m^2 - 1}) - 1 \right]$$

*Oblate Spheroid*

$$N = \frac{2\pi}{m^2 - 1} \left( \frac{m^2}{\sqrt{m^2 - 1}} \arcsin \frac{\sqrt{m^2 - 1}}{m} - 1 \right)$$

Since for the prolate spheroid the two short axes are equal, and for the oblate case the two long axes are equal, then for either case the demagnetizing factor along the short axis is easily obtained by using the above formulas and the expression for the sum. Formulas and tables for the general ellipsoid have been given by Osborn<sup>1</sup> and Stoner.<sup>2</sup>

For rods magnetized in a uniform field in their long direction, the effective demagnetizing factor at the middle of the rod depends to some extent upon permeability, since permeability affects the distribution of magnetic flux along the rod. Demagnetizing factors for rods have been given by Bozorth and Chapin<sup>3</sup> (see Table 5f-37).

TABLE 5f-37. DEMAGNETIZING FACTORS  $N/4\pi$  FOR RODS\* AND ELLIPSOIDS  
MAGNETIZED PARALLEL TO THE LONG AXIS

Dimensional ratio (length/diameter)	Rod	Prolate ellipsoid	Oblate ellipsoid
0	1.0	1.0	1.0
1	0.27	0.3333	0.3333
2	0.14	0.1735	0.2364
5	0.040	0.0558	0.1248
10	0.0172	0.0203	0.0696
20	0.00617	0.00675	0.0369
50	0.00120	0.00144	0.01472
100	0.00036	0.000430	0.00776
200	0.000090	0.000125	0.00390
500	0.000014	0.0000236	0.001567
1000	0.0000036	0.0000066	0.000784
2000	0.0000009	0.0000019	0.000392

\* Values for the rods were obtained empirically for high-permeability materials.

Demagnetizing fields also play a role in magnetostriction, where the strain in a magnetized body is to some extent dependent upon its shape, the effect being known as the magnetostriction form effect. As calculated by Becker,<sup>4</sup> in an elastically isotropic

<sup>1</sup> J. A. Osborn, *Phys. Rev.* **67**, 351 (1945).

<sup>2</sup> E. C. Stoner, *Phil. Mag.* **36** [7], 803 (1945).

<sup>3</sup> R. M. Bozorth and D. M. Chapin, *J. Appl. Phys.* **13**, 320 (1942).

<sup>4</sup> R. Becker, *Z. Physik* **87**, 547 (1934).

prolate spheroid magnetized parallel to the long axis, the observed longitudinal magnetostriction is greater than that of an infinite rod by the form effect strain,

$$\Delta\lambda = \frac{1}{2} M^2 N \left( \frac{1}{3k} + \frac{a}{2G} \right)$$

where, again,  $M$  is the intensity of magnetization,  $N$  the demagnetizing factor in the long direction,  $k$  the elastic compression modulus,  $G$  the shear modulus, and

$$a = - \frac{1}{N} \frac{\partial N}{\partial e_{11}}$$

$e_{11}$  being the strain in the longitudinal direction. Values for  $a$  are given in Table 5f-38.  $\Delta\lambda$  is usually important only for large values of  $M^2 N$ .

TABLE 5f-38. MAGNETOSTRICTION FORM FACTORS  
(See equation for  $\Delta\lambda$ )

$m = \text{length/diameter}$	$N$	$a$
1	4.19	0.80
2	2.18	1.07
3	1.37	1.23
4	0.95	1.31
5	0.70	1.38
10	0.255	1.53
15	0.135	1.60
20	0.085	1.63
30	0.043	1.68

The volume form effect strain in the above case is

$$\Delta\omega = \frac{M^2 N}{2k}$$

and the transverse strain along the two equivalent short axes is simply  $(\Delta\omega - \Delta\lambda)/2$ . Other cases have been considered by Gersdorf<sup>1</sup> and Carr.<sup>2</sup>

Brown<sup>3</sup> has shown that actually the strains calculated by Becker are only average strains, and in reality the form effect is not a uniform strain but changes from point to point within the ellipsoid. As calculated by Gersdorf,<sup>4</sup> the form-effect strain at the center of a sphere is about twice as great as the average value.

In the case of an elastically anisotropic single crystal, similar but somewhat more complicated expressions apply for the form effect. Of particular interest is the form effect in a disklike oblate single-crystal spheroid magnetized in the equatorial plane. In general, the crystal axes and the principal axes of the ellipsoid will not coincide. For a cubic crystal the average form-effect components to the strain tensor are,<sup>5</sup> for  $i = 1, 2, 3$ ,

$$\begin{aligned} (e_{ii})_{fe} &= \text{const} + (h_1)_{fe} \alpha_i^2 \\ (e_{ij})_{fe} &= \text{const} + (h_2)_{fe} \alpha_i \alpha_j \end{aligned}$$

<sup>1</sup> R. Gersdorf, *Physica* **26**, 553 (1960).

<sup>2</sup> W. J. Carr, Jr., "Handbuch der Physik," vol. 18/2, S. Flügge, ed., Springer-Verlag OHG, Berlin, 1966.

<sup>3</sup> W. F. Brown, Jr., *Revs. Modern Phys.* **25**, 131 (1953).

<sup>4</sup> R. Gersdorf, *Physica* **26**, 553 (1960).

<sup>5</sup> W. J. Carr, Jr., "Handbuch der Physik," vol. 18/2, S. Flügge, ed., Springer-Verlag OHG, Berlin, 1966.

where the components are referred to the cubic crystal axes, and  $\alpha_i$  is the direction cosine of magnetization with respect to the  $i$ th axis,

$$(h_1)_{fe} = -\frac{F}{3} \frac{M^2}{c_{11} - c_{12}}$$

$$(h_2)_{fe} = -\frac{F}{6} \frac{M^2}{c_{44}}$$

with  $c_{11}$ ,  $c_{12}$ , and  $c_{44}$  the elastic constants; and  $F$  defined by

$$F = \frac{3\pi}{2\epsilon^3} \left[ (1 - \epsilon^2)(3 + 2\epsilon^2) - \frac{3}{\epsilon} (1 - \epsilon^2)^{\frac{1}{2}} \arcsin \epsilon \right]$$

$\epsilon$  being the eccentricity, defined in terms of the principal axes  $a$ ,  $b$ ,  $c$  of the ellipsoid by

$$\epsilon = \frac{c}{(1 - \epsilon^2)^{\frac{1}{2}}}$$

The constants in the equations for the form-effect strains depend upon the orientation of the ellipsoid with respect to crystal axes, but are independent of the direction of magnetization, which takes any direction within the plane of the disk.