Magnetic Anisotropy. A Reformulation and its Consequences[1])

by **E. Ascher**

Battelle Institute, Advanced Studies Center, Geneva, Switzerland

(25. V. 66)

Summary. The consequences of the relation between ferromagnetism and symmetry are analyzed. It is found that the usual anisotropy coefficients are rather intricate entities, but that their accurate measurement reveals the Shubnikov point group of the crystal. A change of preferential direction turns out to be a first-order phase transition. Hidden properties of ferromagnetic crystals are foreseen, among which piezomagnetism and optical rectification.

In this paper we want to take seriously some (almost) trivial relations between ferromagnetism and symmetry and to show that they give rise to some non-trivial consequences.

1.

There is something disturbing about the fact that the direction of spontaneous magnetization in a ferromagnetic crystal is usually calculated by minimizing the free energy for a symmetry that – by hypothesis – does not permit any spontaneous magnetization. This practice can certainly be justified, but it seldom is, or if so, inadequately.

Let us clarify a first point concerning the form of the density of free energy of the crystal, i.e. after deduction of the contribution of the vacuum. This is usually called the magnetocrystalline energy or anisotropy energy. Consider a cubic crystal. Up to terms of sixth power in the magnetization, there are four possible expressions (and not only one) for the Helmholz free energy[2]), namely:

$$F_1 = K_0 + K_1 (M_x^2 M_y^2 + M_y^2 M_z^2 + M_z^2 M_x^2) + K_2 M_x^2 M_y^2 M_z^2 + \dots \tag{I}$$

$$F_2 = F_1 + K_3 (M_x^4 M_y^2 + M_y^4 M_z^2 + M_z^4 M_x^2) \tag{II}$$

$$F_3 = F_1 + K' M_x M_y M_z \tag{III}$$

$$F_4 = F_1 + K_3 (M_x^4 M_y^2 + M_y^4 M_z^2 + M_z^4 M_x^2) + K' M_x M_y M_z . \tag{IV}$$

---

[1]) Dedicated to the memory of Professor A. PERRIER.

[2]) DÖRING [1][3]) has determined the purely electric contributions to the free energy for the ordinary crystal classes. His result may be extended to the Shubnikov crystal classes and to vectors of other types. SIROTIN [2] has done this for the magnetic case, but not for all Shubnikov classes. A complete survey is contained in a forthcoming technical report [3], which contains also the expressions for a third type of vector, viz. velocity or current density [4]. See also Appendix 1.

[3]) Numbers in brackets refer to References, page 476.

These four possibilities are distributed among the sixteen cubic Shubnikov crystal classes in the following way:

I: 432, $\bar{4}3\,m$, $m\,3\,m$, $4321'$, $m'\,3\,m'$, $\bar{4}3\,m\,1'$, $m'\,3\,m$, $m\,3\,m\,1'$

II: $231'$, $m'\,3$, $m\,31'$

III: $4'\,32'$, $\bar{4}'\,3\,m'$, $m\,3\,m'$

IV: 23, $m\,3$.

Therefore it is incorrect to say that odd powers are inconsistent with cubic symmetry, and that odd power terms are generally absent in the expression for any symmetry. True, odd terms are absent in the expression for any paramagnetic crystal; however, in cubic antiferromagnetic crystals, for instance, the magnetocrystalline energy may obviously contain terms of all odd powers, except the first one[4]).

A first-order term is contained in the magnetocrystalline energy of a ferromagnetic crystal, by definition. This, however, can never be the case in a cubic crystal. Therefore a domain of a ferromagnetic crystal that we are used to call cubic, can never have cubic symmetry. When a cubic crystal becomes ferromagnetic, it ceases to be cubic.

2.

It is well known that any ferromagnetic substance necessarily belongs to one of the thirty-one Shubnikov crystal classes that admit an invariant magnetization vector. We shall call the corresponding groups M-groups. The Shubnikov point groups that may arise in a transition from a given paramagnetic or antiferromagnetic state into a ferromagnetic one may be found by determination of the maximal M-subgroups of the Shubnikov group of the original state[5]).

At the same time one obtains of course the possible direction of easy magnetization for the original symmetry, without calculating extrema (see also [4] and [6]).

Take, for instance, a cubic crystal, more precisely a paramagnetic crystal of class $m\,3\,m$ (case of iron and nickel). The Shubnikov crystal class in then $m\,3\,m\,1'$. It is essential to specify the Shubnikov crystal class; not all cubic crystals permit the same directions of easy magnetization and, of course, the domain symmetry depends on the original crystal class (see Appendix 2). The maximal M-subgroups of $m\,3\,m\,1'$ are:

A) $4/m\,m'\,m'$,   B) $\bar{3}\,m'$,   C) $m\,m'\,m'$.

The first is contained three times as maximal M-subgroup (the direction of the corresponding invariant magnetization vectors is also indicated):

A1) $4/m_x\,m'_y\,m'_z$ $M^s = \pm\,M_x$

A2) $4/m_y\,m'_z\,m'_x$ $M^s = \pm\,M_y$

A3) $4/m_z\,m'_x\,m'_y$ $M^s = \pm\,M_z$.

---

[4]) DZIALOSHINSKI [5] was probably the first to point out the fallacy of arguments that use time reversal to prove the general impossibility of some phenomena in crystals, without ascertaining that the symmetry group of the system (crystal) includes this operation. This is certainly not the case for antiferromagnetic or ferromagnetic crystals.

[5]) A maximal M-subgroup is an M-subgroup that is not contained in any other M-subgroup.

This describes, for instance, iron at room temperature; the preferential directions are the three [100] directions; the symmetry of a domain is $4/m\,m'\,m'$. Nickel above $\sim 200\,°C$ has the same preferential directions and consequently, since the paramagnetic crystal class is the same, also the same symmetry.

The group $\bar{3}\,m'$ is contained four times as maximal M-subgroups[6]):

B1) $\bar{3}_\alpha\,m'$ $M^s = \pm\,M_\alpha$ B3) $\bar{3}_\gamma\,m'$ $M^s = \pm\,M_\gamma$

B2) $\bar{3}_\beta\,m'$ $M^s = \pm\,M_\beta$ B4) $\bar{3}_\delta\,m'$ $M^s = \pm\,M_\delta$.

This represents the case of nickel at room temperature; the preferential directions are [111], the symmetry is $\bar{3}\,m'$.

The group $m\,m'\,m'$ is contained six times as maximal M-subgroup (there are furthermore six other M-subgroups, but they are not maximal).

C1) $m_a\,m_b'\,m_x'$ $M^s = \pm\,M_a$ C4) $m_d\,m_y'\,m_c'$ $M^s = \pm\,M_d$

C2) $m_b\,m_x'\,m_a'$ $M^s = \pm\,M_b$ C5) $m_e\,m_f'\,m_z'$ $M^s = \pm\,M_e$

C3) $m_c\,m_d'\,m_y'$ $M^s = \pm\,M_c$ C6) $m_f\,m_z'\,m_e'$ $M^s = \pm\,M_f$.

This corresponds to [110] as preferential direction.

Thus, given a paramagnetic or antiferromagnetic Shubnikov crystal class, there corresponds a definite symmetry to each preferential direction and *vice versa*.

3.

Usually the preferential directions are determined from the anisotropy coefficients K (see e.g. [7]). It thus follows that the Shubnikov crystal class of a ferromagnetic compound (with known high-temperature symmetry) may be determined by measuring its anisotropy coefficients. Unfortunately, though not astonishingly, the values of the anisotropy coefficients for a given compound vary significantly from author to author [8].

At certain values of the ratios of the anisotropy coefficients K, there occurs a change of the preferential directions[7]). The uncertainty about the values of the anisotropy constants results in an even greater uncertainty about the transition temperature. These transition temperatures, however, can in principle be determined in a more direct way.

4.

A change of the direction of easy magnetization is a first-order phase transition. Indeed, neither of the symmetry groups corresponding to the two directions of easy magnetization in question is a subgroup of the other. Hence the transition is not a continuous one, and *a fortiori* not a second-order transition.

There is experimental evidence for a phase transition, although, from available date, it is not possible to decide whether the transition is of first or of second order. In nickel the preferential direction at room-temperature is [111]; below the Curie-

---

[6]) The crystallographie directions are abbreviated as follows: $x = [100]$, $y = [010]$, $z = [001]$; $\alpha = [1\bar{1}\bar{1}]$, $\beta = [\bar{1}1\bar{1}]$, $\gamma = [\bar{1}\bar{1}1]$, $\delta = [111]$; $a = [011]$, $b = [0\bar{1}1]$, $c = [101]$, $d = [\bar{1}01]$, $e = [110]$, $f = [\bar{1}10]$.

[7]) For instance in situations adequately described by formula I: $K_2 = -9\,K_1 < 0$ for $[100] \leftrightarrow [111]$; $4\,K_2 = -9\,K_1 > 0$ for $[111] \leftrightarrow [110]$; and $K_2 > 0$, $K_1 = 0$ for $[110] \leftrightarrow [100]$.

temperature it is [100]. KIRKHAM [9] has found at $\sim 200\,°C$ a relative maximum of the initial susceptibility of Ni as a function of temperature. He has attributed the phenomenon to 'a transition at that temperature of the direction of the elementary domain magnetization from [111] to [100]'. The phenomenon appears even more clearly in the measurements of KNELLER [10], whose results are reproduced in Figure 1.
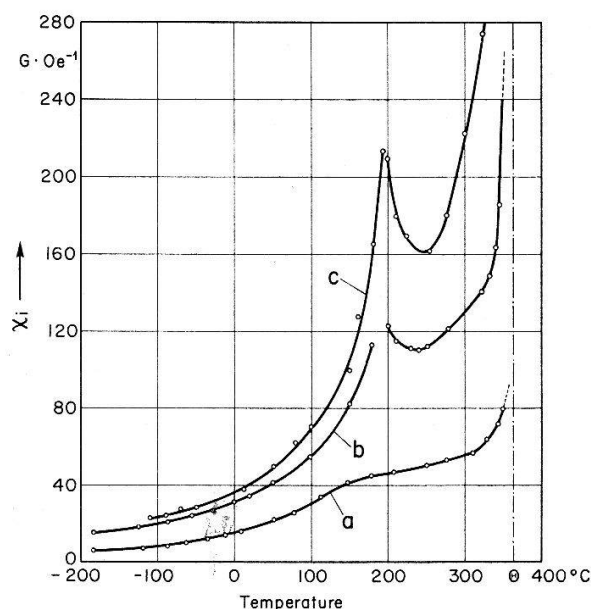

Figure 1

Initial susceptibility of polycrystalline nickel, recrystallized a) at 630 °C, b) at 1000 °C, c) at 1100 °C. After KNELLER [10].

The explanation of the phenomenon given in [10] is quite different from the one proposed here (see also [11]): namely, that the peak of the susceptibility curve at 200 °C reveals a first-order phase transition from the Shubnikov crystal class $\bar{3}\,m'$ to the Shubnikov crystal class $4/m\,m'\,m'$.

5.

It is clear that every ferromagnetic crystal is *a fortiori* piezo-magnetic. But still other phenomena may be predicted to occur in a ferromagnetic crystal, if simply one bears in mind that the symmetry is that of a domain, and not that of the original para- and antiferro-magnetic state.

Let us consider an example. Consider ferromagnetic nickel at room temperature. The symmetry of a domain is $\bar{3}\,m'$. The Gibbs function G contains, among other terms, the following ones:

$$- G = - G_0 + \chi_3 H^3 + \frac{1}{2} \chi_{33} H^3 H^3 + \frac{1}{2} \chi_{11} (H^1 H^1 + H^2 H^2)$$

$$+ \frac{1}{6} \chi_{333} H^3 H^3 H^3 + \frac{1}{6} \chi_{333} H^3 (H^1 H^1 + H^2 H^2)$$

$$+ \frac{1}{6} \chi_{111} H^1 (H^1 H^1 - 3 H^2 H^2) + c_{33} X^{33} + C_{11} (X^{11} + X^{22})$$

$$+ a_{311} H^3 (X^{11} + X^{22}) + a_{131} (H^1 X^{31} + H^2 X^{23})$$

$$+ a_{111} [H^1 (X^{11} - X^{22}) - 2 H^2 X^{12}] + \dots .$$

Here χ_3 represents the spontaneous magnetization (hence the 3-direction is a [111]-direction with respect to the cubic axes of the high-temperature phase). The χ_{ik} are of course, the components of the susceptibility tensor. The χ_{ijk} will be discussed further on. X^{ik} is the stress tensor. The c_{ik} represents the spontaneous strains (of the ferromagnetic phase with respect to the paramagnetic one), and the a_{ijk} are the piezomagnetic coefficients.

From (1) we obtain e.g. for the longitudinal ($\lambda_{\parallel}$) and transverse ($\lambda_{\perp}$) (fractional) change in length in fields parallel to the spontaneous magnetization:

$$\lambda_{\parallel} = c_{33} + a_{333} H\,, \qquad \lambda_{\perp} = c_{11} + a_{311} H\,. \tag{2}$$

This is certainly not in contradiction with experiment (although the interpretation given here is not that which one usually finds in textbooks). Figure 2 shows that in a saturated single crystal of nickel, i.e. when one measures essentially the properties of a domain, the change in length is essentially a linear function of the applied field (piezomagnetism) and not a quadratic one (magnetostriction).
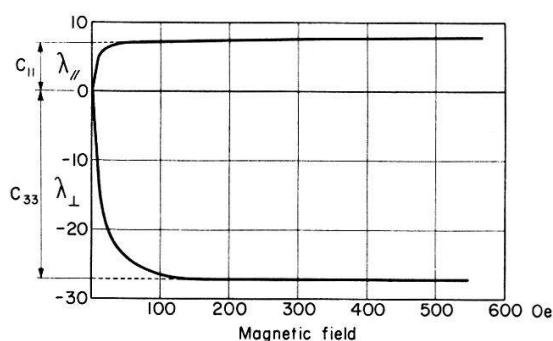

Figure 2

Longitudinal and transverse 'magnetostriction' in single crystals of nickel, magnetic field [111]. After MASIYAMAS results [12] as reproduced in [13].

A linear variation of λ is observed also for other crystals and other directions of the field. However, magnetostriction need not always be negligible with respect to piezomagnetism.

The χ_{ijk} represent the terms in the magnetic susceptibility that depend linearly on the magnetic field. In the same way as in the electrical case, where the analogous terms lead to an electro-optical effect, called the Pockels effect, the χ_{ijk} give rise to a magneto-optical effect that may be called Mockels effect (see Appendix 3). Other known manifestations of these terms, in the electrical case, are harmonic generation and optical rectification [14]. We may expect these effects to occur also in their magnetic equivalent. Here is not the place to discuss these effects in detail, but it should be pointed out that *magnetic* optical rectification could be technically interesting.

6.

The phenomena discussed – as exemples – in the preceding paragraph may be termed 'hidden phenomena'. The meaning is the following. These phenomena occur in a single domain: they can be observed only when the single domain has been experimentally prepared or isolated. In a homogeneous, unprepared single crystal, all

possible domains occur equally. What one then observes is the sum over the domains. Now in the case of nickel, for instance, the sum over the eight possible orientations of the $\bar{3}\,m'$-domains reproduces necessarily the symmetry of the paramagnetic state, namely $m\,3\,m\,1'$.

Thus, formula (1), valid for a single domain, yields

$$- G = - G_0 + \frac{4}{3}\,(\chi_{33} + 2\,\chi_{11})\,(H_x^2 + H_y^2 + H_z^2)$$
$$+ \frac{8}{3}\,(c_{33} + 2\,c_{11})\,(X_{xx} + X_{yy} + X_{zz}) + \ldots$$

an expression that, in accordance with the cubic symmetry $m\,3\,m\,1'$, contains no first and no third-order tensors, but only a term corresponding to the isotropic susceptibility and another that describes the spontaneous deformation of the 'cubic' ferromagnetic phase with respect to the cubic paramagnetic phase.

Similary, when the expressions for the anisotropy energy for the true magnetic symmetry $\bar{3}\,m'$ are summed over the domains, one obtains exactly the expression (I) for the appropriate cubic symmetry. Furthermore, one gets the anisotropy coefficients as linear combinations of the components of the inverse-susceptibility tensors (of orders two, four and six) for the domain (see Appendix 1b). These are the physically relevant constants. The physical interpretation of their combinations seems to be as awkward a task as their reproducible measurement. Indeed, the distribution of domains varies from one real single crystal to another. And while the superposition of the domain always gives the cubic symmetry irrespective of their distribution as long as all orientations are present, the value of the anisotropy coefficients depends on that distribution. Now, the meaning of the usual procedure 'determination of the direction of the spontaneous magnetization that does not allow any' becomes clear. The symmetry that does not allow the spontaneous magnetization is only apparent; it appears because the single crystal has not been resolved into domains.

7.

The phenomena discussed here are a special case of a large class of phenomena that may understood as continuous transitions, the principal characteristics of which are the following. A system being in a state with a definite symmetry is given. The state of the system is a function of a parameter. At a critical value of the parameter, the system is split into subsystems ('domains') of lower symmetry in such a way that the totality of the subsystems still has the original symmetry. Thus the symmetry is not 'broken', but 'broken up' into subsymmetries that are symmetries of the subsystems. Subsymmetries are described by specific subgroups of the group describing the original symmetry (e.g. maximal M-subgroups). A single subsystem breaks the original symmetry. It may be stabilised either through 'preparation' (application of an appropriate field) or through the presence of the other subsystems that are necessary to restore the original symmetry.

Appendix 1: The anisotropy coefficients.

The anisotropy coefficients that appear in formulas (I) to (IV) are in fact somewhat intricate entities.

a

Let us take for instance case IV i. e. the crystal classes 23 and $m\,3$. Up to the sixth order, the following magnetic invariants may be constructed

$$I_2 = M_x^2 + M_y^2 + M_z^2 = M^2 \qquad\qquad I_{61} = M_x^6 + M_y^6 + M_z^6$$

$$I_3 = M_x\,M_y\,M_z \qquad\qquad\qquad\quad I_{62} = M_x^2\,M_y^2\,M_z^2$$

$$I_{41} = M_x^4 + M_y^4 + M_z^4 \qquad\qquad I_{63} = M_x^4\,M_y^2 + M_y^4\,M_x^2 + M_z^4\,M_x^2$$

$$I_{42} = M_x^2\,M_y^2 + M_y^2\,M_z^2 + M_z^2\,M_x^2 \qquad I_{64} = M_x^2\,M_y^4 + M_x^2\,M_z^4 + M_z^2\,M_x^4$$

$$I_5 = M_x\,M_y\,M_z\,(M_x^2 + M_y^2 + M_z^2)$$

Thus the expression for the anisotropy energy becomes

$$\text{(IV')} \quad F_4 = A_0 + B\,M^2 + C\,I_3 + D_1\,I_{41} + D_2\,I_{42} + L\,I_5 + N_1\,I_{61} + N_2\,I_{62}$$
$$+ N_3\,I_{63} + N_4\,I_{64}$$

where the coefficients are components of the tensors of inverse susceptibility of orders two to six. They depend on the temperature T, but not on magnetization. It is clear that the above invariants are not independent. Using the relations that exist among them, Equation (IV') may be simplified; the result is Equation (IV). But let us look at the coefficients K of the equation:

$$K_0 = A_0 + B\,M^2 + D_1\,M^4 + N_1\,M^6 \qquad\qquad K_3 = N_3 - N_4$$

$$K_1 = (D_2 - 2\,D_1) + (N_4 - 3\,N_1)\,M^2 \qquad\qquad K' = C + L\,M^2$$

$$K_2 = 3\,N_1 + N_2 - 3\,N_4$$

Usually the appearance of the equations is further simplified by introducing the direction cosines $\alpha_x,\,\alpha_y,\,\alpha_z$ of the magnetization. (It should not be forgotten however, that these direction cosines are invariant under space inversion.)

$$F_4 = K_0 + \overline{K}_1\,(\alpha_x^2\,\alpha_y^2 + \alpha_y^2\,\alpha_z^2 + \alpha_z^2\,\alpha_x^2) + \overline{K}_2\,\alpha_x^2\,\alpha_y^2\,\alpha_z^2$$
$$+ \overline{K}_3\,(\alpha_x^4\,\alpha_y^2 + \alpha_y^4\,\alpha_z^2 + \alpha_z^4\,\alpha_x^2) + \overline{K'}\,\alpha_x\,\alpha_y\,\alpha_z$$

where now

$$\overline{K}_1 = K_1\,M^4, \quad \overline{K}_2 = K_2\,M^6, \quad \overline{K}_3 = K_3\,M^6, \quad \overline{K}^1 = K'\,M^3$$

The other cubic cases are easily deduced from this:

$$\text{(I):} \quad C = L = 0, \quad N_3 = N_4$$

$$\text{(II):} \quad C = L = 0$$

$$\text{(III):} \quad N_3 = N_4$$

The natural variables for these coefficients thus appear to be T and M^2:

$$\overline{K} = \overline{K}\,(T,\,M^2)\,.$$

Of course, through the dependence of M on H, the anisotropy coefficient depends on T and H

$$\overline{K} = \overline{K}(T,\,M^2(H,\,T))$$

but this dependence is necessarily complicated; still more complications lie ahead.

b

Let us now take into account the fact that the true symmetry for nickel at room temperature is $\overline{3}\,m'$, and not $m\,3\,m\,1'$.

For the former symmetry, the magnetic invariants up to sixth order are:

$$I_1 = M_z$$
$$I_{51} = M_z^5$$
$$I_{21} = M_z^2$$
$$I_{52} = M_z^3\,(M_x^2 + M_y^2)$$
$$I_{22} = M_x^2 + M_y^2$$
$$I_{53} = M_z^2\,M_x\,(M_x^2 + 3\,M_y^2)$$
$$I_{31} = M_z^3$$
$$I_{54} = M_z\,(M_x^2 + M_y^2)^2$$
$$I_{32} = M_z\,(M_x^2 + M_y^2)$$
$$I_{55} = M_x\,(M_x^2 + M_y^2)\,(M_x^2 - 3\,M_y^2)$$
$$I_{33} = M_x\,(M_x^2 - 3\,M_y^2)$$
$$I_{61} = M_z^6$$
$$I_{41} = M_z^4$$
$$I_{62} = M_z^4\,(M_x^2 + M_y^2)$$
$$I_{42} = M_z^2\,(M_x^2 + M_y^2)$$
$$I_{63} = M_z^3\,M_x\,(M_x^2 - 3\,M_y^2)$$
$$I_{43} = M_z\,M_x\,(M_x^2 - 3\,M_y^2)$$
$$I_{64} = M_z^2\,(M_x^2 + M_y^2)^2$$
$$I_{44} = (M_x^2 + M_y^2)^2$$
$$I_{65} = M_z\,M_x\,(M_x^2 + M_y^2)\,(M_x^2 - 3\,M_y^2)$$
$$I_{66} = (M_x^2 + M_y^2)^3$$
$$I_{67} = M_x^2\,(M_x^2 - 3\,M_y^2)^2$$

Thus the expression for the anisotropy energy becomes

$$F = a_0 + a_1\,I_1 + b_1\,I_{21} + b_2\,I_{22} + c_1\,I_{31} + c_2\,I_{32} + c_3\,I_{33}$$
$$+ d_1\,I_{41} + d_2\,I_{42} + d_3\,I_{43} + d_4\,I_{44} + h_1\,I_{51} + h_2\,I_{52} + h_3\,I_{53} + h_4\,I_{44}$$
$$+ h_5\,I_{55} + n_1\,I_{61} + n_2\,I_{62} + n_3\,I_{63} + n_4\,I_{64} + n_5\,I_{65} + n_6\,I_{66} + n_7\,I_{67}\,.$$

The coefficients, the components of the inverse susceptibilities of orders one to six, depend on the temperature, but not on the magnetization. They are of course not independent. When the above expression is summed over the eight domains with magnetizations $\pm M_\alpha$, $\pm M_\beta$, $\pm M_\gamma$, and $\pm M_\delta$, respectively (of which equal volumes are supposed to be present), one obtains (I') (i.e. (IV') with $C = L = 0$, and

$N_4 = N_5 = N_3$); however the coefficients relative to the cubic symmetry are now expressed as combinations of those belonging to the domain symmetry:

$$A_0 = 8\,a_0$$

$$B = \frac{8}{3}\,(b_1 + 3\,b_2)$$

$$D_1 = \frac{8}{9}\,(d_1 + 3\,d_2 + 9\,d_4)$$

$$D_2 = \frac{8}{3}\,(2\,d_1 + 9\,d_4)$$

$$N_1 = \frac{8}{27}\,(n_1 + 3\,n_2 + 9\,n_4 + 27\,n_6)$$

$$N_2 = \frac{1}{3}\,[80\,n_1 + 72\,(n_4 - n_7)]$$

$$N_3 = \frac{1}{9}\,[40\,(n_1 + n_2) + 216\,n_6 + 72\,n_7]$$

c

It is known -- see e.g. [7] and [8] – that minimizing the anisotropy energy for the high-temperature symmetry yields also preferential directions of the magnetization that do not coincide with the direction of any crystallographic axis of that symmetry. From the theory presented here it follows that a preferential direction necessarily coincides with the direction of a crystallographic axis. Nevertheless the theory accounts also for the above-mentioned deviations.

Indeed, since a change of the direction of easy magnetization is a first-order phase transition, both phases, i.e. both preferential directions, may coexist at the temperature of phase transition. In a real material, the transition temperature is smeared out. (This is illustrated also by Figure 1. Furthermore, it would be interesting to take explicitly into account the magnetic interaction between the phases.) Thus there is a temperature region where the preferential direction is intermediate between two crystallographic directions, the exact orientation depending on the ratio (of the volumes) of the two phases present.

Appendix 2: Maximal M-subgroups of the cubic Shubnikov point groups and corresponding preferential directions.
A list of all maximal P-, M-, and j-subgroups of all Shubnikov point groups may be found in [3].

SHUVALOV [15] has published a list of possible Shubnikov groups in ferromagnetic transitions. He supposes known the high temperature symmetry and the direction of spontaneous magnetization after the transition. For these latter, he admits any direction with respect to the crystallographic axes of the high-temperature phase. In the present work, possible directions of spontaneous magnetization are not supposed but found, and it turns out that the spontaneous magnetization cannot be directed in any direction other than that of a symmetry axis of the high-temperature phase, and furthermore that not all of these directions are necessarily allowed. Thus Shuvalov's list contains necessarily more transitions than ours. (But Shuvalov

Groups	Preferential directions		
	x, y, z	a, b, c, d, e, f	$\alpha, \beta, \gamma, \delta$
23	2		3
$m\,3$	$2/m$		$\bar{3}$
$231'$	$22'\,2'$		3
$m'\,3$	$m'\,m'\,2$		3
$m\,31'$	$m'\,m'\,m$		$\bar{3}$
432	4	2	3
$\bar{4}3\,m$	$\bar{4}$	m	3
$4'\,32$	$22'\,2'$		$32'$
$4'\,3\,m'$	$m'\,m'\,2$		$3\,m'$
$m\,3\,m$	$4/m$	$2/m$	$\bar{3}$
$4321'$	$42'\,2'$	$22'\,2'$	$32'$
$m'\,3\,m'$	$4\,m'\,m'$	$m'\,m'\,2$	$3\,m'$
$m\,3\,m'$	$m'\,m'\,m$		$\bar{3}\,m'$
$\bar{4}3\,m\,1'$	$\bar{4}2'\,m'$	$m'\,m\,2'$	$3\,m'$
$m'\,3\,m$	$\bar{4}2'\,m'$	$m'\,m\,2'$	$32'$
$m\,3\,m\,1'$	$4/m\,m'\,m'$	$m'\,m'\,m$	$\bar{3}\,m'$

intentionally has not considered all possible high-temperature groups.) For the discussion of the intermediate directions of spontaneous magnetization that sometimes seem to occur, see the discussion Appendix 1c.

SIROTIN [16] has also determined, by yet another method and under more restrictive conditions, the possible changes in ferromagnetic transitions. His list contains, necessarily, fewer transitions than ours.

Appendix 3: Magnetic optical rectification.

Consider the following term in the development of the Gibbs function

$$- G = \ldots + \frac{1}{6}\,\chi_{ijk}(\omega', \omega'', \omega''')\,H^i(\omega')\,H^j(\omega'')\,H^k(\omega''') + \ldots$$

Here $H(\omega')$, $H(\omega'')$, and $H(\omega''')$ are three magnetic fields of frequencies ω', ω'', and ω''' respectively.

The tensor $\chi_{ijk}(\omega', \omega'', \omega''')$ – the third order generalised susceptibility – is obviously invariant under the permutations of the couples (i, ω'), (j, ω''), and (k, ω''').

Concerning the derivations of G, four cases must be distinguished.

(i) $\omega' \neq \omega''$, $\omega'' \neq \omega'''$, $\omega''' \neq \omega'$

$$- \frac{\partial G}{\partial H^i(\omega')} = M_i(\omega') = \frac{1}{6}\,\chi_{ijk}(\omega', \omega'', \omega''')\,H^j(\omega'')\,H^k(\omega''')$$

(ii) $\omega'' = \omega''' = \omega$

$$M_i(\omega') = \frac{1}{6}\,\chi_{ijk}(\omega', \omega, \omega)\,H^j(\omega)\,H^k(\omega).$$

This case comprises second harmonic generation and optical rectification, since for

$$H^j(\omega) = h^j \sin \omega\, t, \quad H^k(\omega) = h^k \sin \omega\, t$$

one finds

$$M_i(\omega') = M_i(0) + M_1(2\,\omega)$$

$$= \frac{1}{12}\,\chi_{ijk}(\omega',\omega,\omega)\,h^j\,j^k - \frac{1}{6}\,\chi_{ijk}(\omega',\omega,\omega)\,h^j\,h^k\cos 2\,\omega\,t.$$

The notation in Reference [14] is

$$X^0_{ijk} = \frac{1}{12}\,\chi_{ijk}(\omega',\omega,\omega)\,.$$

(iii) $\omega' = \omega''' = \omega$

$$M_i(\omega) = \frac{1}{3}\,\chi_{ijk}(\omega,\omega',\omega)\,H^j(\omega')\,H^k(\omega)\,.$$

This case is adequate for the description of different variants of the Mockels effect. In [14]:

$$X^\omega_{ijk} = \frac{1}{3}\,\chi_{ijk}(\omega,\omega',\omega)\,.$$

(iv) $\omega' = \omega'' = \omega''' = \omega$

$$M_i(\omega) = \frac{1}{2}\,\chi_{ijk}(\omega,\omega,\omega)\,H^j(\omega)\,H^k(\omega)\,.$$

This case describes the ordinary third-order D.C. ($\omega = 0$) or A.C. susceptibility.

The general invariance of $\chi_{ijk}(\omega',\omega'',\omega''')$ implies in particuliar $\chi_{ijk}(\omega',\omega,\omega) = \chi_{ikj}(\omega',\omega,\omega) = \chi_{jik}(\omega,\omega',\omega) = \chi_{kij}(\omega,\omega',\omega)$ so that

$$X^0_{ijk} = \frac{1}{2}\,X^\omega_{jik}$$

or also

$$(X^0_{ijk} + X^0_{ikj}) = \frac{1}{4}\,(X^\omega_{jik} + X^\omega_{kij}) = \frac{1}{2}\,X^\omega_{jik}.$$

This relation, found by WARD and FRANKEN [17], and recently verified experimentally by WARD [18], is thus a direct consequence of the definitions of the coefficients.

References

[1] DÖRING, W., Ann. Phys. (7) *1*, 102 (1958).
[2] SIROTIN, Yv. I., Sov. Phys.-Crystallography *7*, 71 (1962).
[3] Properties of Shubnikov Point Groups, Battelle Technical Report.
[4] ASCHER, E., Helv. phys. Acta *39*, 40 (1966).
[5] DZIALOSHINSKI, I. E., Sov. Phys.-JETP *6*, 621 (1958).
[6] ASCHER, E., Phys. Letters *20*, 352 (1966).
[7] SMIT, J., WIJN, H. P. J., Ferrites, Philips Technical Library, 1959.
[8] KRAUSE, D., phys. stat. sol. *6*, 125 (1964) especially footnotes [3]) and [4]).
[9] KIRKHAM, D., Phys. Rev. *52*, 1162 (1937).
[10] KNELLER, E., in *Beiträge zur Theorie des Ferromagnetismus und der Magnetisierungskurve*, edited by W. Köster, Springer, Berlin, Göttingen und Heidelberg 1956, p.110.
[11] KNELLER, E. *Ferromagnetismus*, Springer Verlag, Berlin, Göttingen und Heidelberg 1962, p. 551.
[12] MASIYAMA, Y., Sci. Repts. Tôhoku Imp. Univ. *17*, 945 (1928).
[13] BOZORTH, R. M., *Ferromagnetism*, van Nostrand, Toronto, New York and London 1951.
[14] BASS, M., FRANKEN, P. A., WARD, J. F., Phys. Rev. *138*, A534 (1965).
[15] SHUVALOV, L. A., Sov. Phys.-Crystallography *4*, 371 (1959).
[16] SIROTIN, Yv. I., Sov. Phys.-Crystallography *8*, 195 (1963).
[17] WARD, J. F., FRANKEN, P. A., Phys. Rev. *133*, A183 (1964).
[18] WARD, J. F., Phys. Rev. *143*, 569 (1966).