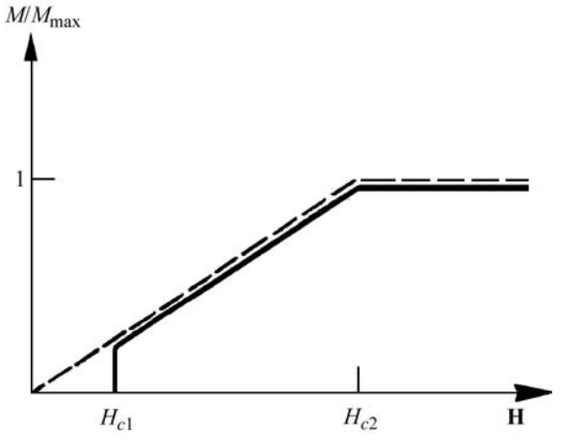

Fig. 1.5.3.7. Dependence of the relative magnetization M/M_{max} on the magnetic field at $T = 0$. The dashed line corresponds to $\mathbf{H} \perp Oz$, the full line to $\mathbf{H} \parallel Oz$. H_{c1} is the field of spin-flop, H_{c2} is the field of spin-flip.

second-order phase transitions starting from the thermodynamic potential $\tilde{\Phi}$ and taking into account that L is small and $DL^2 \ll B$ close to T_N.

In the presence of the magnetic field $\mathbf{H} \perp Oz$, $\mathbf{L}$ is parallel to Oz, $\mathbf{LM} = 0$, the coefficient A at L^2 is replaced by $A + 2D'H^2/B^2$ and the latter is zero at the new transition point. The critical field is given by the relation

$$H_{c2}^2 = (\lambda B^2/2D')(T_N - T), \quad \mathbf{H} \perp Oz. \tag{1.5.3.46}$$

If the field is applied parallel to the z axis, then $\mathbf{L}$ remains parallel to Oz if $H < H_{c1}$ ($H_{c1} \simeq aB^2/D$ in the neighbourhood of T_N). Therefore,

$$H_{c2}^2 = \frac{\lambda B^2}{2(D + D')}(T_N - T), \quad \mathbf{H} \parallel Oz,\ H < H_{c1}. \tag{1.5.3.47}$$

If $H > H_{c1}$, $\mathbf{L}$ becomes perpendicular to the z axis and the anisotropy term has to be taken into account:

$$H_{c2}^2 = \frac{\lambda B^2}{2D'}(T_N - T - a/\lambda), \quad \mathbf{H} \parallel Oz,\ H > H_{c1}. \tag{1.5.3.48}$$

Formulas (1.5.3.46)–(1.5.3.48) show that the transition temperature is reduced by applying the magnetic field. The displacement of the transition point is directly proportional to the square of the applied field. Fig. 1.5.3.9 shows the phase diagram of an antiferromagnet in the neighbourhood of T_N. Unlike ferromagnets, antiferromagnets maintain the second-order phase transition when a magnetic field is applied because the symmetry

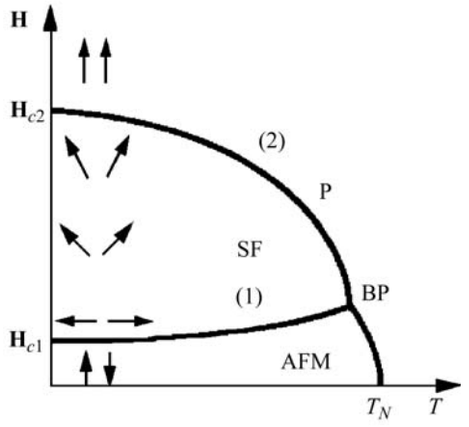

Fig. 1.5.3.8. Magnetic phase diagram for a uniaxial antiferromagnet in a magnetic field applied parallel to the axis. (1) The line of spin-flop transition (H_{c1}); (2) the line of spin-flip transition (H_{c2}); P, paramagnetic phase; AFM, easy-axis antiferromagnetic phase; SF, spin-flop phase; BP, bicritical point.

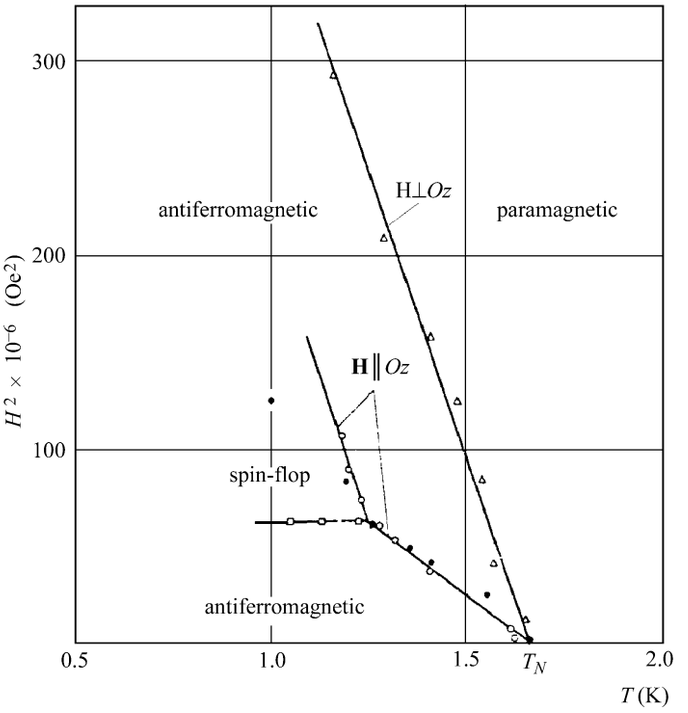

Fig. 1.5.3.9. Phase diagram for a uniaxial antiferromagnet in the proximity of T_N, calculated for $MnCl_2{\cdot}4H_2O$. Experimental data are taken from Gijsman *et al.* (1959). The ordinate value 100 corresponds to H = 10 kOe, *i.e.* B = 10 kG = 1 T.

of the crystal in the antiferromagnetic state differs essentially from that in the paramagnetic state also if the crystal is placed into a magnetic field.

Formula (1.5.3.43) describes the magnetization process only in easy-axis antiferromagnets. For easy-plane antiferromagnets, the anisotropy in the plane is usually extremely small and the antiferromagnetic vector rotates freely in the basic plane. Therefore, for any direction of the magnetic field, the vector $\mathbf{L}$ becomes aligned perpendicular to the applied magnetic field. Correspondingly the magnetization becomes

$$\mathbf{M} = \chi_z H_z \hat{\mathbf{z}} + \chi_\perp H_\perp \hat{\mathbf{x}}, \tag{1.5.3.49}$$

where $\hat{\mathbf{z}}$ and $\hat{\mathbf{x}}$ are unit vectors parallel and perpendicular to the axis.

1.5.4. Domain structure

1.5.4.1. *180° domains*

Neither symmetry nor energy considerations can determine the alignment of the magnetization vector $\mathbf{n}$ in a non-chiral easy-axis magnet (of ferro- or antiferromagnetic type). The vector $\mathbf{n}$ may be aligned parallel or antiparallel to the positive direction of the z axis. Therefore, specimens of any magnet are usually split into separate regions, called domains. In each domain of an easy-axis magnet, the vector $\mathbf{n}$ has one of its two possible directions. Such domains are called 180° domains. Adjacent domains are separated by a domain wall, in which the magnetic moments are no longer strictly parallel (or antiparallel). As a result of this, both the exchange and the anisotropy energy rise inside the volume of the domain wall.

In ferromagnets (and ferrimagnets), the gain in the exchange and anisotropy energy in a multidomain sample is compensated by the loss in the magnetostatic energy. The existence of the domain structure is responsible for the behaviour of a ferromagnet in an applied magnetic field. There are two kinds of magnetization processes that one has to distinguish: the displacement of the domain walls and the rotation of the spontaneous

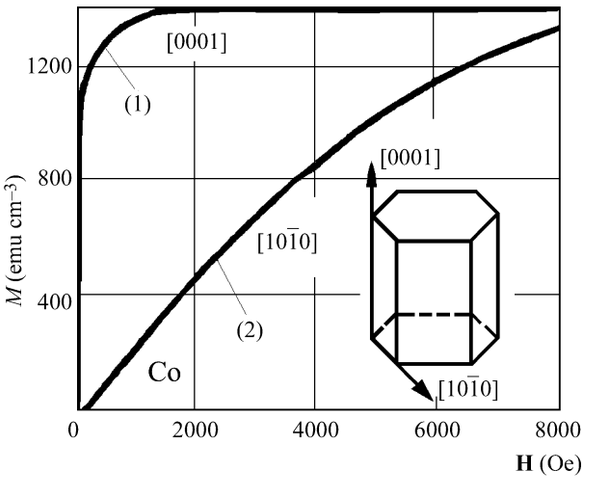

Fig. 1.5.4.1. Magnetization curves of hexagonal cobalt for two main crystallographic directions: (1) [0001] and (2) [10$\bar{1}$0]. (1 Oe = $10^3/(4\pi)$ A m^{-1}; 1 emu cm^{-3} = 10^3 A m^{-1}.)

magnetization vector from the easy direction to the direction of the applied magnetic field. The magnetization process will first be considered without taking the demagnetizing field into account. If the magnetic field is applied parallel to the axis of an easy-axis ferromagnet, the displacement of the domain wall will completely determine the magnetization process. If the sample contains no impurities and crystal defects, such a displacement must take place in an infinitely small magnetic field [see curve (1) in Fig. 1.5.4.1 and Fig. 1.5.4.3*a*]. If the magnetic field is applied perpendicular to the easy axis, the size of the domains does not change but their magnetization vectors rotate. Let us denote the spontaneous magnetization by M_s. Then the sample magnetization M rises linearly with respect to the applied magnetic field:

$$M = \mu_0^* H M_s^2/(2K_1), \qquad (1.5.4.1)$$

where K_1 is defined by relations (1.5.3.8)–(1.5.3.10). Some nonlinearity in H can arise from the fourth-order term with K_2 [see curve (2) in Fig. 1.5.4.1 and Fig. 1.5.4.3*c*]. When $H = 2K_1/(\mu_0^* M_s) = H_s$, the magnetizations of all the domains are rotated by 90° and the magnetization of the sample becomes oriented along the magnetic field; its value is saturated and is equal to the spontaneous magnetization M_s. If $T \neq 0$ K, there is an additional rise in magnetization with the magnetic field. This rise, which is called true magnetization, is relatively very small at all temperatures except for the temperature region close to the transition temperature. If the magnetic field is applied at an arbitrary angle θ to the easy axis, the magnetization process occurs in two steps [see curves (2) in Fig. 1.5.4.2 and Fig. 1.5.4.3*b*]. First, as a result of the wall displacement, the magnetization jumps to the value M_1 in a small magnetic field. Next, the rotation process follows and at H_s the sample becomes saturated [see curves (2) in Fig. 1.5.4.2]. It is essential to take the shape of the sample into account in considering the problem of the magnetization processes in ferromagnets, as the demagnetizing field can be up to $4\pi M$ in Gaussian units, up to M in SI units. In real materials, the displacement process is partly (at low fields) reversible and partly (at higher fields) irreversible. Therefore, complicated hysteresis processes arise in magnetizing ferromagnets.

The problem of 180° domains in antiferromagnets is not as clear. These domains differ in the sign of the antiferromagnetic vector **L**. This vector was defined as the difference of the vectors of sublattice magnetizations in a two-sublattice antiferromagnet, *i.e.* $\mathbf{M}_1 - \mathbf{M}_2$. Thus two such antiferromagnetic domains differ only by the numbering of the sites in the sublattices. Antiferromagnetic 180° domains are also called S-domains. The wall between two S-domains is schematically represented in Fig. 1.5.4.4.

The origin of the antiferromagnetic S-domains cannot be explained from the point of view of energy balance as in a ferromagnet. These domains give rise to additional exchange and anisotropy energies which are not compensated by a decrease of any other kind of energy. Thus the S-domain structure is thermodynamically not stable. However, experiments show that S-domains exist in most easy-axis antiferromagnets.

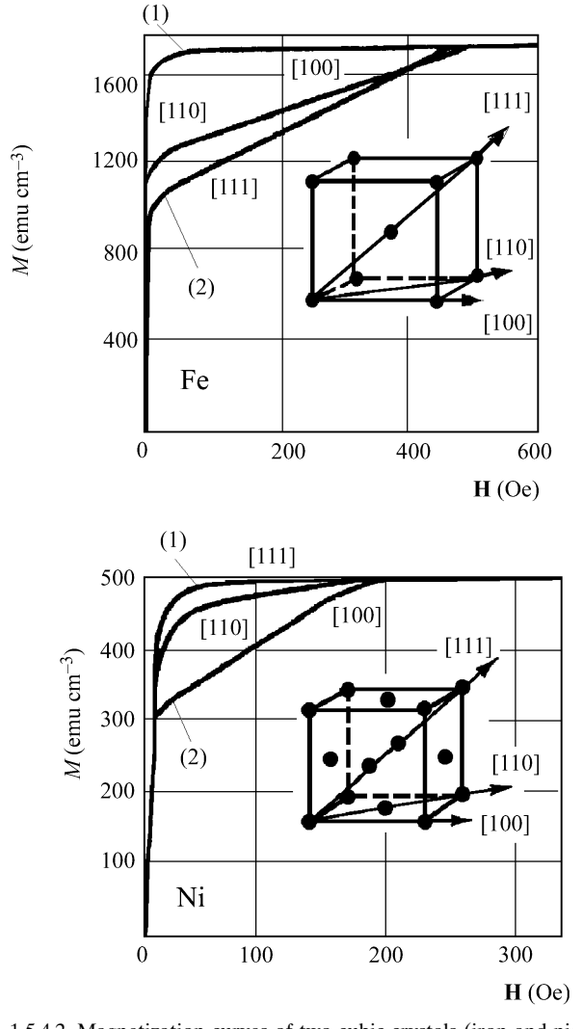

Fig. 1.5.4.2. Magnetization curves of two cubic crystals (iron and nickel) for three crystallographic directions. (1 Oe = $10^3/(4\pi)$ A m^{-1}; 1 emu cm^{-3} = 10^3 A m^{-1}.)

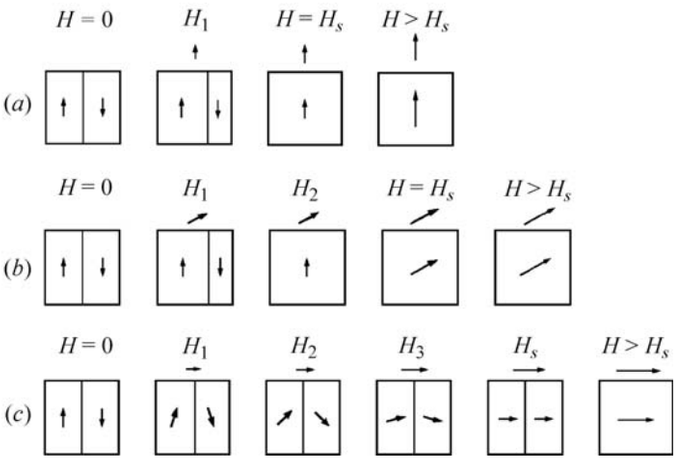

Fig. 1.5.4.3. Schematic display of the magnetization: (*a*) H along the easy axis; (*b*) H at an arbitrary angle to the easy axis; (*c*) H perpendicular to the easy axis.

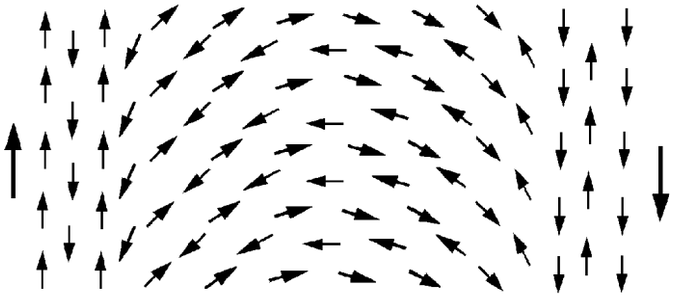

Fig. 1.5.4.4. A 180° domain wall in an antiferromagnet.

The formation of S-domains can be explained by assuming that when the material is cooled down to the Néel temperature, antiferromagnetic ordering arises in different independent regions. The direction of the vector **L** in these regions is accidental. When growing regions with different directions of **L** meet, the regular alternation of the directions of magnetic moments of the ions is broken on the border between these regions. Domain walls are created on such borders. Such domain structures can be metastable.

The existence of S-domains in easy-axis antiferromagnets was first proved in experiments in which effects that depend on the sign of **L** were investigated. These are piezomagnetism, linear magnetostriction and the linear magnetoelectric effect. The sign of these effects depends on the sign of **L**. We shall discuss this problem in detail in Sections 1.5.7 and 1.5.8. Later, 180° domain walls were observed in neutron scattering experiments (Schlenker & Baruchel, 1978), and the domains themselves in magneto-optical experiments (see Kharchenko *et al.*, 1979; Kharchenko & Gnatchenko, 1981).

1.5.4.2. *Twin domains*

As pointed out in Section 1.5.3, in tetragonal non-easy-axis magnets, in easy-plane hexagonal and trigonal and in cubic magnets there is more than one easy magnetization direction (3, 4 or 6). As a result, domains arise in which vectors $\mathbf{M}_s$ or **L** are directed to each other at 120, 109.5, 90, 70.5 and 60°. Such domains are called twin or T-domains. The formation of magnetic T-domains is accompanied by the formation of crystallographic domains as a result of spontaneous magnetostriction. But mostly this is very small. Each of the T-domains may split into 180° domains.

The magnetization process in ferromagnets possessing T-domains is similar to the previously described magnetization of an easy-axis ferromagnet in a magnetic field directed at an oblique angle. First the displacement process allows those 180° domains that are directed unfavourably in each T-domain to disappear, and then the rotation process follows.

In easy-plane antiferromagnets, the T-domain structure is destroyed by a small magnetic field and the antiferromagnetic vector **L** in the whole specimen becomes directed perpendicular to the applied magnetic field, as was explained in Section 1.5.3.

There are four kinds of T-domains in cubic antiferromagnets, in which the vectors **L** are directed parallel or perpendicular to the four ⟨111⟩ axes. Such a T-domain structure can be destroyed only when the applied magnetic field is so strong that the antiferromagnetic order is destroyed at a spin-flip transition.

1.5.4.3. *Ferroic domains*

Aizu (1970) gave a classification of domain formation when a crystal undergoes a transition from an unordered to a magnetically ordered state that has a lower point-group symmetry (see also Section 3.1.1). The unordered state (called the prototype phase) has a grey point group. The number of elements in this group is equal to the product of the number of elements in the point group of the ordered state (called the ferroic state) times the number of domains. Aizu found that there are 773 possible combinations of the point-group symmetries of the prototype and the ferroic state, if crystallographically inequivalent orientations of the subgroup in the group of the prototype are distinguished. These 773 combinations are called ferroic species and are characterized by a symbol giving first the point group of the prototype, then the letter F, then the point group of the ferroic state and finally a letter between parentheses if different orientations are possible. As an example, the $2'$ axis of the ferroic state is parallel to the fourfold axis of the prototype in $4221'\mathrm{F}2'(p)$ and perpendicular to it in $4221'\mathrm{F}2'(s)$.

Let us discuss the ferroic states of rhombohedral transition-metal oxides given in Table 1.5.3.4. The paramagnetic prototype has point group $\bar{3}m1'$. The four monoclinic ferroic species have six domains ('orientation states') each, which form three pairs of 180° domains ('time-conjugate orientation states'). All four species are 'fully ferroelastic', *i.e.* the three pairs show different orientations of the spontaneous strain; two of the four species ($\bar{3}m1'\mathrm{F}2'/m'$ and $\bar{3}m1'\mathrm{F}2/m$) are also 'fully ferromagnetic' because all six domains have different orientations of the spontaneous magnetization. Switching a domain into another with a different orientation of the spontaneous strain can be achieved by applying mechanical stress. If the domain was spontaneously magnetized, the orientation of the magnetization is changed simultaneously. Similarly, a domain can be switched into another with a different orientation of the spontaneous magnetization by means of a magnetic field. If the two spontaneous magnetizations have different directions (not just opposite sign), the direction of the spontaneous strain will change at the same time.

Aizu's concept of ferroic species has been extended by Litvin (2009) from ferroelectric, ferromagnetic (or antiferromagnetic) and ferroelastic domains to the occurrence of domains bearing a toroidal moment, *i.e.*, to ferrotoroidic domains (Van Aken *et al.*, 2007). It is noteworthy that this extension leaves the number of Aizu's 773 species unchanged. This is plausible, since ferrotoroidic domains are simultaneously either ferromagnetic or purely antiferromagnetic. In both cases the toroidal moment is an inseparable part of the spin structure. Owing to this coupling, toroidic domains can be time-reversed either by a magnetic field alone or by electric and magnetic fields, depending on the tensor form of the linear magnetoelectric effect (Schmid, 2008).

The Aizu classification is of interest for technological applications because it gives an overall view not only of domain formation but also of the possibilities for domain switching.

1.5.5. Weakly non-collinear magnetic structures

As was indicated above (see Tables 1.5.3.3 and 1.5.3.6), certain magnetic space groups allow the coexistence of two different types of magnetic ordering. Some magnetic structures can be described as a superposition of two antiferromagnetic structures with perpendicular antiferromagnetic vectors $\mathbf{L}_\alpha$. Such structures may be called weakly non-collinear antiferromagnets. There can also be a superposition of an antiferromagnetic structure **L** with a ferromagnetic one **M** (with $\mathbf{L} \perp \mathbf{M}$). This phenomenon is called weak ferromagnetism. We shall demonstrate in this section why one of the magnetic vectors has a much smaller value than the other in such mixed structures.

1.5.5.1. *Weak ferromagnetism*

The theory of weak ferromagnetism was developed by Dzyaloshinskii (1957*a*). He showed that the expansion of the thermodynamic potential $\tilde{\Phi}$ may contain terms of the following type: $L_i M_k$ $(i, k = x, y)$. Such terms are invariant with respect to the transformations of many crystallographic space groups (see Section 1.5.3.3). If there is an antiferromagnetic ordering in the material $(L_i \neq 0)$ and the thermodynamic potential of the