

1.5. MAGNETIC PROPERTIES

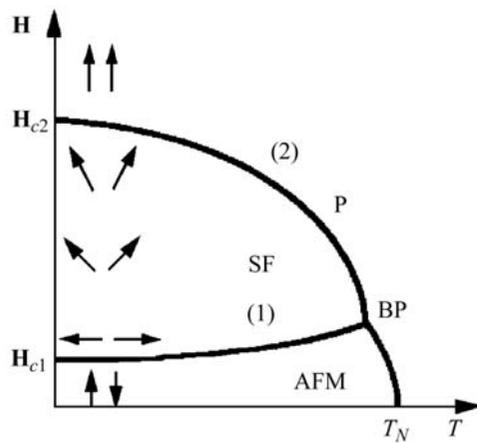


Fig. 1.5.3.8. Magnetic phase diagram for a uniaxial antiferromagnet in a magnetic field applied parallel to the axis. (1) The line of spin-flop transition (H_{c1}); (2) the line of spin-flip transition (H_{c2}); P, paramagnetic phase; AFM, easy-axis antiferromagnetic phase; SF, spin-flop phase; BP, bicritical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

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

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 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

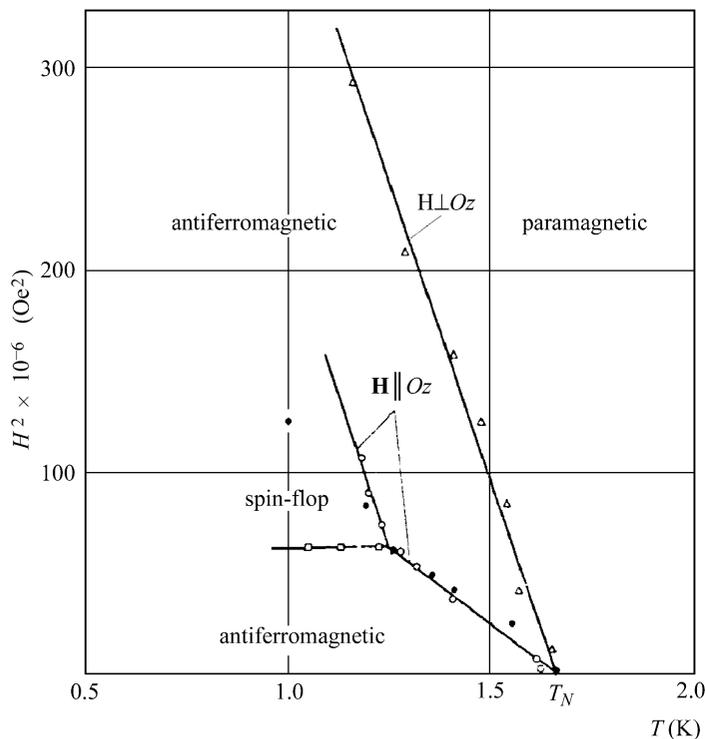


Fig. 1.5.3.9. Phase diagram for a uniaxial antiferromagnet in the proximity of T_N , calculated for $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$. Experimental data are taken from Gijssman *et al.* (1959).

aligned perpendicular to the applied magnetic field. Correspondingly the magnetization becomes

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

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 magnetic (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 magnetic are usually split into separate regions called domains. In each domain of an easy-axis magnetic, 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 loss in the exchange and anisotropy energy in a multidomain sample is compensated by the gain 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 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. 1.5.4.3a]. 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:

$$M = HM_s^2/2K_1, \quad (1.5.4.1)$$

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. 1.5.4.3c]. When $H = 2K_1/M_s = H_s$, 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. 1.5.4.3b]. 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 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.

1. TENSORIAL ASPECTS OF PHYSICAL PROPERTIES

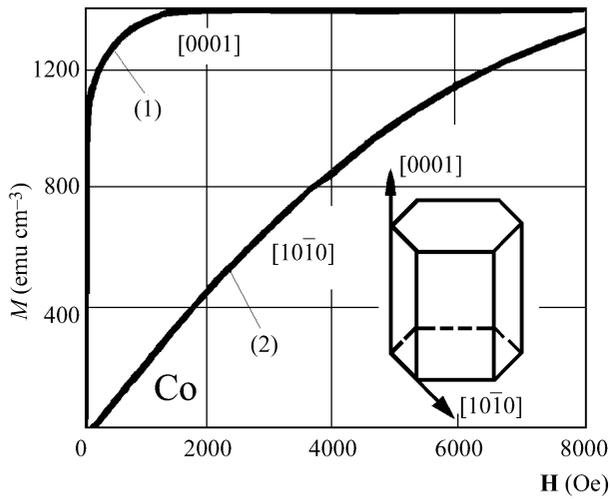


Fig. 1.5.4.1. Magnetization curves of hexagonal cobalt for two main crystallographic directions: (1) [0001] and (2) [10 $\bar{1}$ 0].

The problem of 180° domains in antiferromagnets is not clear. These domains differ in the sign of the antiferromagnetic vector \mathbf{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.

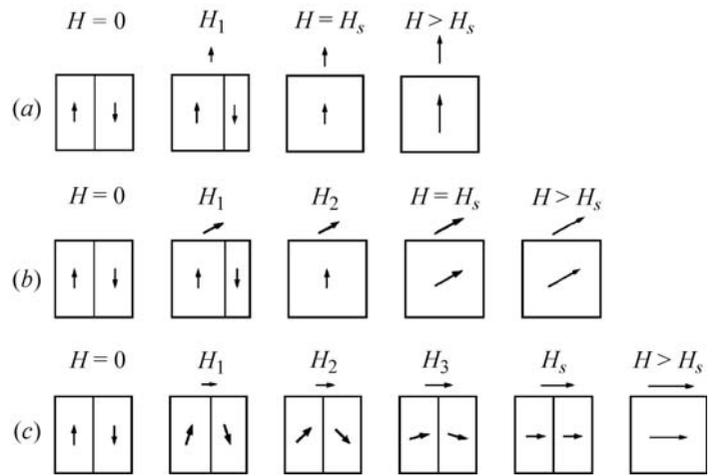


Fig. 1.5.4.3. Schematic display of the magnetization: (a) along the easy axis; (b) at an arbitrary angle to the easy axis; (c) perpendicular to the easy axis.

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.

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 \mathbf{L} in these regions is accidental. When growing regions with different directions of \mathbf{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 \mathbf{L} were investigated. These are piezomagnetism, linear magnetostriction and the linear magnetoelectric effect. The sign of these effects depends on the sign of \mathbf{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).

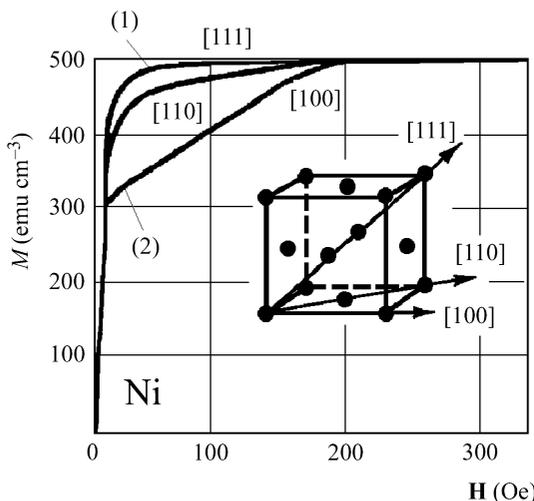
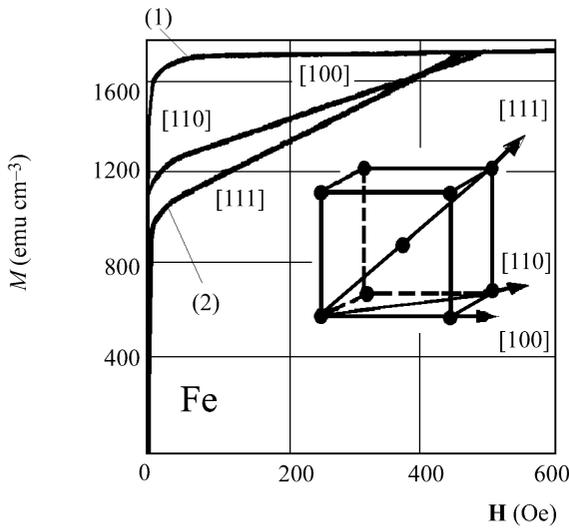


Fig. 1.5.4.2. Magnetization curves of two cubic crystals (iron and nickel) for three crystallographic directions.

1.5.4.2. Twin domains

As pointed out in Section 1.5.3, in tetragonal non-easy-axis magnetics, in easy-plane hexagonal and trigonal and in cubic magnetics there is more than one easy magnetization direction (3, 4 or 6). As a result, domains arise in which vectors \mathbf{M}_s or \mathbf{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

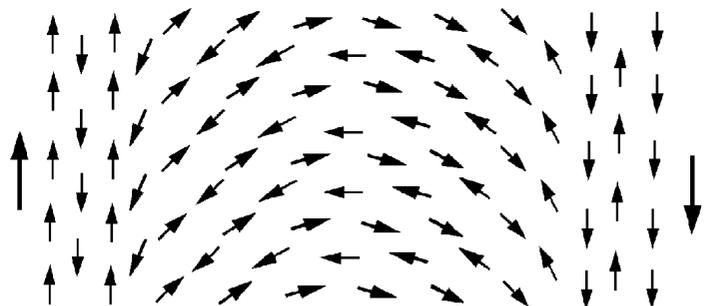


Fig. 1.5.4.4. A 180° domain wall in an antiferromagnet.

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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 \mathbf{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 \mathbf{L} are directed parallel or perpendicular to the four $\langle 111 \rangle$ 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'F2'(p) and perpendicular to it in 4221'F2'(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 ($\bar{3}m1'F2'/m'$ and $\bar{3}m1'F2/m$) 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.

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}_α . Such structures

may be called weakly non-collinear antiferromagnets. There can also be a superposition of an antiferromagnetic structure \mathbf{L} with a ferromagnetic one \mathbf{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 (1957a). 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 material contains such a term, the minimum of the potential will be obtained only if $M_k \neq 0$ as well. The term $L_i M_k$ is a relativistic one. Therefore this effect must be small.

We shall consider as an example the origin of weak ferromagnetism in the two-sublattice antiferromagnets MnCO_3 , CoCO_3 and NiCO_3 , discussed in Section 1.5.3.1. The following analysis can be applied also to the four-sublattice antiferromagnet $\alpha\text{-Fe}_2\text{O}_3$ (assuming $\mathbf{L}_1 = \mathbf{L}_2 = 0$, $\mathbf{L}_3 = \mathbf{L}$). All these rhombohedral crystals belong to the crystallographic space group $D_{3d}^6 = R\bar{3}c$. The thermodynamic potential $\tilde{\Phi}$ for these crystals was derived in Section 1.5.3.3. For the case of a two-sublattice antiferromagnet, one has to add to the expression (1.5.3.26) the invariant (1.5.3.24):

$$\tilde{\Phi} = (A/2)\mathbf{L}^2 + (B/2)\mathbf{M}^2 + (a/2)L_z^2 + (b/2)M_z^2 + d(L_x M_y - L_y M_x) - \mathbf{M}\mathbf{H}. \quad (1.5.5.1)$$

The coefficients of the isotropic terms (A and B) are of exchange origin. They are much larger than the coefficients of the relativistic terms (a, b, d). Minimization of $\tilde{\Phi}$ for a fixed value of \mathbf{L}^2 and $\mathbf{H} = 0$ gives two solutions:

(1) $\mathbf{L} \parallel Oz$ ($L_x = L_y = 0$, $\mathbf{M} = 0$). FeCO_3 and the low-temperature modification of $\alpha\text{-Fe}_2\text{O}_3$ possess such purely antiferromagnetic structures.

(2) $\mathbf{L} \perp Oz$ [$M_x = (d/B)L_y$, $M_y = (d/B)L_x$, $M_z = 0$]. This structure exhibits a spontaneous ferromagnetic moment

$$M_D = (M_x^2 + M_y^2)^{1/2} = (d/B)L. \quad (1.5.5.2)$$

The magnetic moment M_D is smaller than the magnetization of the sublattices ($M_0 = L/2$) in the ratio $2d/B$. This phenomenon is therefore called weak ferromagnetism. The vectors \mathbf{M}_D and \mathbf{L} are mutually perpendicular. Their direction in the plane is determined by the sixth-order terms of the anisotropy energy (see Section 1.5.3.2). This anisotropy is extremely small in most materials. The vectors of magnetization of the sublattices \mathbf{M}_0 are deflected by a small angle $\varphi \simeq 2d/B$ away from the direction of the antiferromagnetic axis \mathbf{L} in such weak ferromagnets (see Fig. 1.5.5.1).

Weak ferromagnetism was first observed in the following trigonal crystals: the high-temperature modification of haematite, $\alpha\text{-Fe}_2\text{O}_3$ (Townsend Smith, 1916; Néel & Pauthenet, 1952), MnCO_3 (Borovik-Romanov & Orlova, 1956) and later also in CoCO_3 , NiCO_3 and FeBO_3 . In accordance with theory, weak ferromagnetism does not occur in trigonal crystals with a positive anisotropy coefficient a . Such crystals become easy-axis antiferromagnets. Of this type are FeCO_3 and the low-temperature modification of $\alpha\text{-Fe}_2\text{O}_3$. For four-sublattice antiferromagnets, the sequence of the directions of the magnetic moments of the sublattices is also essential. For example, the structures of the types \mathbf{A}_1 and \mathbf{A}_2 (see Fig. 1.5.3.4 and Table 1.5.3.3) do not exhibit weak ferromagnetism.