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Application of the Ferromagnetic Resonance Method in the Study of Heterogeneous Catalysts

A.A.Slinkin

The main features of the ferromagnetic resonance method are discussed in the context of the study of heterogeneous catalysts. Results obtained by this method are examined, and possible future developments are pointed out.

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I. INTRODUCTION

A detailed knowledge of the physical properties and structure of real catalysts is one of the prerequisites for the development of a theory of heterogeneous catalysis able to pave the way to the synthesis of catalysts of prescribed chemical composition and structure, leading to the development of new chemical processes and to the improvement of existing ones. Unfortunately, and in spite of the large number of catalysts used in industry and in laboratories, this information is lacking in most cases. Only during the last 10–15 years, as a result of the application of various physical methods, has some progress been possible in this direction. The study of a real, multicomponent heterogeneous catalyst by physical methods is a very complex problem. A catalyst of this type contains a very large number of defects, frequently of unknown nature. In these circumstances, quantitative interpretation of the results of physical measurements becomes very difficult, and quantitative calculations are ambiguous. The position is made worse by the change in both the number and the nature of the defects induced by the catalytic reaction itself. A study of these systems would be meaningless to a solid-state physicist concerned with studies at the single-crystal level. Yet, we are forced to work with these materials if we wish to inquire into the nature of heterogeneous catalysis.

At the moment, the only way out of the dilemma is to examine a given catalyst by the greatest possible number of physical methods which, by cross-checking and complementing each other, can offer a fuller understanding of the real physical structure of heterogeneous catalysts. Therefore, the use of any physical method which can reveal new facets in the study of catalyst structure is highly desirable. Accordingly, this review will deal with the ferromagnetic resonance method and its application to the study of various nickel catalysts.

II. THE FERROMAGNETIC RESONANCE METHOD

1. General Remarks

Static magnetic methods have been applied for a number of years to the study of catalysts [1-5], with valuable results for both paramagnetic and ferromagnetic catalysts. The application of static magnetic methods (i.e. the measurement of magnetic properties in constant fields) to the analysis of the structure and valency characteristics of paramagnetic ions depends essentially on the use of the Langevin equation and Curie's law.

In paramagnetic materials the magnetic moments of the ions, atoms, or molecules are pointing in all directions in space with equal probability, and the total magnetic moment is zero. When such a material is placed in a magnetic field the magnetic moments become oriented along the field, and the number of moments oriented with the field becomes greater than the number oriented against the field. As a result, the material becomes magnetised, and we observe a positive magnetic susceptibility.

Noting that the magnetic moments in a paramagnetic material immersed in a magnetic field of intensity H are experiencing simultaneously the randomising effect of thermal motion and the orienting effects of the field, Langevin obtained a formula relating the magnetisation to the field strength (H) and to the absolute temperature (T):

$$\sigma = \sigma_0 \left[\coth \frac{\mu H}{kT} - \frac{kT}{\mu H} \right], \qquad (1)$$

where σ is the magnetisation per unit weight of the material, σ_0 the limiting magnetisation per unit weight (saturation magnetisation), μ the magnetic moment of the ion, atom, or molecule, H the field strength in Oersteds, k Boltzmann's constant, and T the absolute temperature.

Fig. 1 shows the variation of the Langevin function with the value of the parameter $\mu H/kT$. It is obvious that the function tends to saturate at high values of H (i.e. tends to the value σ_0). However, with paramagnetic materials fields in excess of 10^6 Oe, which are inaccessible in practice, are needed to reach the saturation region, i.e. to obtain values of $\mu H/kT > 1$. The only way to obtain a Langevin curve covering a significant range of the parameter $\mu H/kT$ with paramagnetic materials is to work at low temperatures and relatively high field strengths. Thus, at $T \simeq 1°K$ and $H \simeq 10^4$ Oe, $\mu H/kT \simeq 1$. More commonly, at room temperature and fields of the order of 10^3 Oe, the value is

$$\mu H/kT = \frac{0.93 \cdot 10^{-20} \cdot 10^4}{1.38 \cdot 10^{-16} \cdot 300} \simeq 0.02, \text{ i.e. } \mu H \ll kT.$$

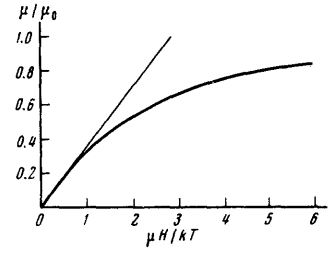


Figure 1. Dependence of the relative magnetic moment μ/μ_0 upon the parameter $\mu H/kT$.

In this case we can expand the Langevin function into a series for small values of the parameter $\mu H/kT$, and retain only the first term of the expansion, giving

$$\sigma = \sigma_0 \frac{\mu H}{3kT} \qquad (2)$$

which is the tangent to the curve of Fig. 1, or

$$\sigma = N\mu \frac{\mu H}{3kT},$$

where N is the number of magnetic particles of magnetic moment μ in 1 g of the material.

$$\chi = \frac{\sigma}{H} = \frac{N\mu^2}{3kT} \quad \text{or} \quad \chi T = C \qquad (3)$$

is Curie's law, where χ is the magnetic susceptibility.

Thus, we obtain Curie's law, where the Curie constant $C = \frac{N\mu^2}{3k}$. However, it must be stressed that Langevin obtained his formula on the assumption that: 1) we are dealing with a gas of paramagnetic particles, and 2) the magnetic moments of the particles are not mutually interacting. In practice, however, plots of $\frac{1}{\chi}$ against T do not pass through the origin as required by formula (3), and χ is found to vary with temperature by the more complicated law

$$\chi = \frac{C}{T - \Delta} \qquad (4)$$

(the Curie–Weiss law), where Δ can be either positive or negative.

This deviation from Curie's law arises from the interaction of the magnetic moments of neighbouring particles, and the constant Δ (Weiss's constant) characterises the magnitude of this interaction in the simplest cases. Nevertheless, the forces between neighbouring ions, atoms, or molecules in paramagnetic materials are not very large, and their magnetic susceptibilities are negligible.

In addition to the static magnetic methods of investigating paramagnetic catalysts, the methods of microwave spectroscopy have come to the fore in recent years, and in particular the electron paramagnetic or electron spin resonance (ESR) method. Details of the method and of the results obtained in studies of heterogeneous catalysts have been discussed elsewhere[6,7]. The resonance conditions for the ESR method are given in the form

$$h\nu = g\mu_B H_0$$

where h is Planck's constant, ν the frequency of the radiation absorbed, g the spectroscopic splitting factor, μ_B is the Bohr magneton, and H_0 the external magnetic field.

We can recast this formula in terms of angular Bohr frequencies:

$$h\nu = \hbar\omega_{res} = g\mu_B H_0, \text{ or}$$
$$\omega_{res} = \gamma H_0, \qquad (5)$$

where

$$\omega_{res} = 2\pi\nu; \quad \gamma = \frac{g\mu_B}{\hbar}, \text{ and } \hbar = \frac{h}{2\pi}.$$

In general, and like the static magnetic susceptibility method, the ESR method when applied to the study of paramagnetic materials relates to the spin and orbital moments of isolated particles (for example, highly dilute solid solutions of paramagnetic ions in a diamagnetic matrix), or alternatively to the relatively weak interactions of the magnetic moments of neighbouring particles.

A situation different in principle is observed in studies of resonance phenomena in ferromagnetics[8]. Because of the very strong exchange interaction between atoms in a ferromagnetic crystal, the magnetic moments of neighbouring atoms are oriented parallel to each other even in the absence of a field, and the application of a field produces gigantic values of the magnetisation (10^4–10^5 times higher than in paramagnetics). The magnetisation process will be considered in more detail in the following sections. The existence of strong exchange interactions, and various other effects, in ferromagnetic substances makes the interpretation of ferromagnetic resonance spectra in polydisperse systems much harder than the interpretation of ESR spectra. Thus, formula (5) must be written, for the case of ferromagnetic resonance, in the form

$$\omega_{res} = \gamma H_{eff}, \qquad (6)$$

where $H_{eff} = H_0 + H'$, and H' is some additional field whose value depends on the nature of the specimen, the experimental conditions, the shape of the particles, the presence of defects, and so on. Failure to allow for this additional field can lead to serious errors, particularly in the determination of the g-factor.

We shall now discuss the main factors which determine the resonance conditions in ferromagnetics, and on the basis of this analysis we shall review the work on the study of catalysts by this method.

2. Influence of Crystallographic Magnetic Anisotropy on the Resonance Frequency and on ΔH

The *magnetic crystallographic anisotropy* effect is one of the most important factors which determine the resonance frequency, and the line width (ΔH) of ferromagnetic resonance, in studies of polydisperse systems. Basically, the nature of the effect is as follows. Let us consider the magnetisation of single crystals of Ni, Fe, and Co as a function of the applied external field and its orientation with respect to the crystal axes. As Fig. 2 shows, an axis along which the crystal can most easily be magnetised exists in these crystals (as also in other ferromagnetics). For example, for Ni this axis is the [111] axis or body diagonal of the cube. The major planes of a cubic crystal and the directions of the corresponding axes are shown in Fig. 3.

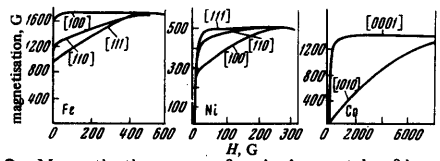


Figure 2. Magnetisation curves for single crystals of iron, nickel, and cobalt.

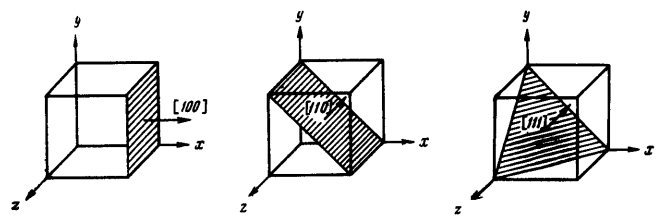


Figure 3. Main crystal planes and axes in a cubic crystal.

How does magnetisation of a magnetically anisotropic crystal occur? If the external magnetic field is parallel to the easy magnetisation axis, the crystal is magnetised practically to saturation in very small fields. If, on the other hand, the direction of magnetisation by the external field is at a definite angle to the easy magnetisation axis, a greater expenditure of energy is required to magnetise the crystal to saturation, and therefore saturation is reached at higher magnetic fields. The physical explanation of the existence of magnetic anisotropy depends on spin–orbital interactions in the crystal. An atom (or ion) in the crystal experiences crystal fields having a definite symmetry, which lead to the removal of orbital degeneracy and therefore to an anisotropic distribution of orbital magnetic moments. The spin magnetic moments (which are mainly responsible for ferromagnetism) are affected by this anisotropic distribution through spin–orbital coupling.

The magnetic anisotropy energy is expressed by the magnetic anisotropy constants, which are strongly temperature dependent. Fig. 4 shows the temperature variation of the first magnetic anisotropy constants (K_1) of Ni, Fe, and Co. It can be seen that the magnetic anisotropy constant is greatest for Co, and that the constants for Ni and Fe are relatively lower. The most striking feature of the temperature dependence of K_1 for nickel is a rapid decrease with increase of temperature, the constant K_1 almost vanishing at 100°. [Unless stated otherwise, all temperatures are in °C (Ed. of Translation).]

How are the conditions for ferromagnetic resonance affected by these peculiarities of the magnetisation of ferromagnetic crystals? It is obvious that if the magnetic

field H_0 is applied in the direction of the axis of easy magnetisation the anisotropy energy will be a minimum. For the case of an Ni single crystal, in which $K_1 < 0$, it has been shown[9] that when $\Theta = 0°$ (difficult magnetisation axis, [100]) we have

$$\frac{\omega_{res}}{\gamma} = H_0 - \frac{2(K_1)}{\sigma_0}, \qquad (7)$$

where σ_0 is the saturation magnetisation and K_1 is the anisotropy constant.

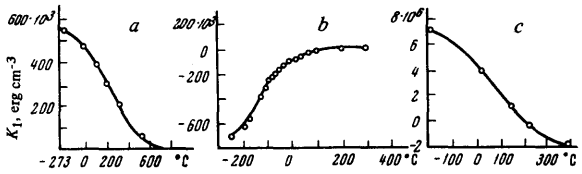


Figure 4. Temperature dependence of the first anisotropy constant (K_1):
a) Fe; *b*) Ni; *c*) Co.

When $\Theta = 54°44'$ (easy magnetisation axis, [111])

$$\frac{\omega_{res}}{\gamma} = H_0 + \frac{4}{3}\frac{(K_1)}{\sigma_0}, \qquad (8)$$

In these formulae the constant external field H_0 together with the additional field resulting from anisotropy,

$$2\frac{(K_1)}{\sigma_0} \quad \text{or} \quad \frac{4}{3}\frac{(K_1)}{\sigma_0},$$

constitute the effective field H_{eff} used in formula (6). Thus, with single crystals it is possible to find H_{eff} and to calculate ω_{res} by experimentally varying the angle between the direction of H_0 and the crystal axes.

In studies of real catalysts we are not dealing with single crystals. One commonly deals with Ni microcrystals in a diamagnetic or paramagnetic matrix ($Ni-Al_2O_3$, $Ni-SiO_2$, $Ni-Cr_2O_3$, etc.) or with highly disperse nickel powders (Raney nickel). In these systems the Ni crystallites have arbitrary orientations of the easy magnetisation axis with respect to the direction of the external field H_0, resulting in a range of resonance fields (at a fixed value of ω) for the various Ni crystallites. This causes significant line broadening, and often produces asymmetry in the shape of the line and a shift of the *g*-factor. This is one of the forms which non-uniform magnetisation of the sample can take.

Obviously, if $K_1 = 0$ and no other sources of non-uniform magnetisation are present, it follows from formulae (7) and (8) that $H_{eff} = H_0$, and formula (5) can be applied. From this formula, which is characteristic for paramagnetic resonance, the *g*-factor can be accurately calculated. Hence, the only way of avoiding the magnetic anisotropy effect in studies of polydisperse catalysts is to measure the ferromagnetic resonance at high temperatures, when $K_1 \simeq 0$ and the *g*-factor can be calculated by formula (5).

3. Influence of Shape Anisotropy on the Resonance Frequency and ΔH

In addition to the non-uniformity of magnetisation due to magnetic crystallographic anisotropy, the true internal magnetic field H_{eff} in a ferromagnetic sample differs from the external magnetic field H_0 through the influence of the geometrical shape of the sample. The physical basis of this effect can be explained as follows. If a sample having a high magnetisation is placed in the uniform external field H_0, magnetic charges giving rise to a formal magnetic field H_e in opposition to the external field H_0 are generated on the surface of the specimen (Fig. 5). This field, called the demagnetising field, is proportional to the magnetisation of the specimen:

$$H_e = -N\sigma_0, \qquad (9)$$

where N is the demagnetisation factor.

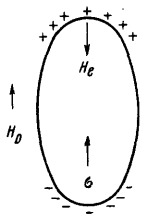


Figure 5. Formation of the demagnetising field H_e.

Hence, the field experienced by the specimen is not H_0 but a field H_{eff} given by

$$H_{eff} = H_0 - N\sigma_0 = H_0 - N\chi H,$$

whence

$$H_{eff} = \frac{1}{1+\chi N} H_0.$$

Since ferromagnetics have very high χ values, the field H_{eff} can differ very substantially from H_0. Strictly speaking, formula (9) is applicable only to ellipsoidal specimens of other shapes. The factor N in formula (9) is the total demagnetisation factor, but it is more convenient to consider factors of the form N_x, N_y, and N_z along the principal semi-axes of the ellipsoid l_x, l_y, and l_z. The relationship between N_x, N_y, and N_z is

$$N_x + N_y + N_z = 4\pi.$$

Allowing for the demagnetising effect of the surface, Kittell obtained the following formula for the resonance frequency

$$\frac{\omega_{res}}{\gamma} = \sqrt{[H_0 + (N_x - N_z)\sigma_0][H_0 + (N_y - N_z)\sigma_0]} \qquad (10)$$

showing that the resonance condition depends on the shape of the specimen and on σ_0. Thus, if we are considering a specimen whose shape is an ellipsoid of revolution about the *z*-axis ($l_x = l_y = l_\perp$; $l_z = l_\parallel$), it follows that $N_x = N_y = N_\perp$ and $N_z = N_\parallel$, so that formula (10) becomes

$$\omega_{res} = \gamma(H_0 - \sigma_0 \Delta N), \quad \text{and} \quad \Delta N = N_\parallel - N_\perp.$$

A graphical expression for the dependence of the shape anisotropy factor ΔN on the ratio of the longitudinal to the radial axes of the ellipsoid $\left(n = \frac{l_\parallel}{l_\perp}\right)$ can be obtained[9] (see Fig. 6).

If follows from the graph that only in the case of a sphere ($n = 1$) does the effect of shape anisotropy on the resonance condition vanish, leading to formula (5), i.e.

$$\omega_{res} = \gamma H_0.$$

The shape of the sample has a very substantial effect on the value of the applied field corresponding to resonance. Thus, for iron (with $\sigma_0 = 1700$ G), the following resonance fields have been observed[9] using specimens of different shape (frequency 10^4 MHz, $\lambda \simeq 3$ cm).

Sphere	$H_{res} \simeq 3570$ Oe
Disk∥	$H_{res} \simeq 530$ Oe
Cylinder⊥	$H_{res} \simeq 12500$ Oe
Disk⊥	$H_{res} \simeq 26800$ Oe.

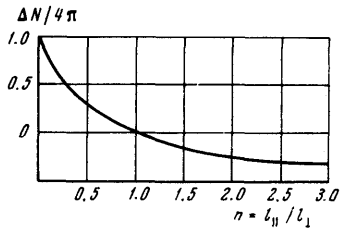


Figure 6. Variation of the difference between the longitudinal and the radial demagnetisation factor of an ellipsoid of revolution with the ratio of the half-axes.

Since a catalyst may contain particles of widely different shape, line broadening can occur through the increased range of resonance fields. However, unlike the broadening caused by magnetic crystallographic anisotropy, this type of broadening should be relatively insensitive to the measurement temperature, since the distribution of particle shapes during measurements of the temperature dependence of line width should remain essentially constant (provided that sintering is not taking place). Extremely interesting in this context is an attempt[10] to investigate the shape of ferromagnetic cobalt particles from the shape of the line. The ferromagnetic resonance of a polycrystalline Co–Cu alloy containing 2% of Co was measured as a function of aging at high temperatures. The calculated shapes of the resonance curve for disordered assemblies of plates, spheres, and rods are shown in Fig. 7*a*. Inspection of the shape of the resonance curves with increasing time and temperature of heat treatment (Fig. 7, *b*–*d*) shows that the particles are almost spherical in the original alloy, but they become larger and plate-like during aging. Thus, the shape of the ferromagnetic particle can be inferred from the features of the resonance curve if due allowance is made for all the other factors which influence the trend of the curve.

4. Domain Structure, Superparamagnetism, and Relaxation Processes

We have already noted the presence in ferromagnetics of strong exchange interactions as a result of which the magnetic moments of the atoms take up parallel directions. We shall now examine in greater detail the magnetisation of ferromagnetic substances. Generally speaking, a ferromagnetic could be expected to be fully magnetised at temperatures below the Curie point even in the absence of a field. Such, however, is not the case, and the modern theory of ferromagnetism offers the following explanation. Consider a ferromagnetic single crystal which has become spontaneously magnetised to saturation in the absence of an external field (Fig. 8*a*). This crystallite can be treated as a permanent magnet, giving rise to a surrounding magnetic field containing an appreciable amount of magnetic energy. However, any system must tend towards a state of minimum free energy. Can this happen in our case? Evidently, if the ferromagnetic crystallite is broken into a number of regions such that the total magnetisation in each pair of neighbouring regions points in opposite directions, the volume occupied by the external magnetic field and the energy of the field will decrease as the number of these regions increases (Figs. 8*b* and 8*c*). A region having only one direction of magnetisation, i.e. a region magnetised to saturation, is called a *domain*. This type of domain structure in ferromagnetic materials results in the magnetic moments at the boundaries between neighbouring domains being oriented in different directions. However, a state in which the magnetic moments are oriented in the same direction is energetically favourable in ferromagnetics. Therefore, energy must be expended to produce opposing orientations of the magnetic moments in the boundary region between domains. This energy is termed the *energy of the domain wall* †. Thus, the fragmentation of a ferromagnetic crystallite into domains involves both a decrease in the energy of the magnetic field outside the crystal and an expenditure of energy in the formation of domain walls. Hence, domain formation will continue until the energy required to form an additional domain becomes equal to the decrease in energy of the magnetic field outside the crystal.

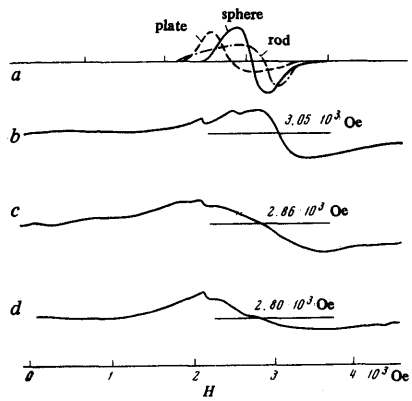


Figure 7. Theoretical and experimental ferromagnetic resonance lines for a Co–Cu (2% Co) alloy[10];
a) theoretical shape of the curve for particles of various shapes;
b) 30 min aging at 600°, average size of Co particles 25 Å;
c) 15 h aging at 600°, average size of Co particles 65 Å;
d) 20 min aging at 800°, average size of Co particles 300 Å.

Fig. 9 is a schematic representation of the magnetisation of a ferromagnetic crystal including its domain structure. In a real crystal the magnetisations of adjacent domains are oppositely oriented, and the total magnetisation is zero (Fig. 9*a*). Upon the application of an external magnetic field, the domains which happen to be magnetised in the

† The inversion of the direction of the magnetic moment at the boundary between domains does not occur abruptly, i.e. within the limits of one atomic layer, but gradually, and it involves hundreds of atomic layers. Therefore the thickness of the boundary wall can be as large as several hundred Ångstroms.

direction of the external field grow at the expense of other domains with a less favourably oriented magnetisation, leading to a movement of the domain walls (Fig. 9*b*). This process is accompanied by an increase in magnetisation. In small magnetic fields the displacement of the domain walls is reversible, and the magnetisation returns to zero when the field is removed. A much more complex situation obtains when large magnetic fields are used. Real crystals invariably contain defects, dislocations, impurities, etc. When a moving domain wall meets one of these defects its progress becomes uneven, discontinuous, and accompanied by a loss of magnetisation energy. As a result, this part of the curve becomes irreversible. Lastly, in large fields, when some domains have already grown at the expense of others and the magnetisation of the former is directed along the field, there are some residual domains whose magnetisation does not coincide with the direction of the applied field (Fig. 9*c*). Larger fields are needed to coerce the magnetic moments of these domains into the direction of the external magnetic field. The overall magnetisation curve is shown in Fig. 10.

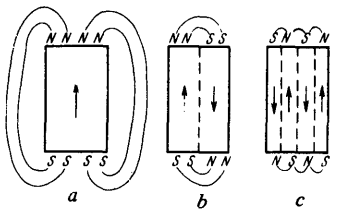


Figure 8. Formation of a domain structure.

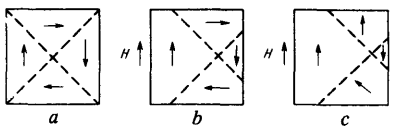


Figure 9. Magnetisation of a ferromagnetic with participation of the domain structure.

So far we have been concerned with a single crystal of a ferromagnetic material subdivided into domains. Real ferromagnetic materials are not usually monocrystalline (particularly in the case of ferromagnetic catalysts), but rather an assembly of a large number of crystallites of various sizes. According to its size, each crystallite is divided into a larger or smaller number of domains. The structure of a real ferromagnetic of this type is shown in Fig. 11. It is evident that its magnetisation can be treated in the same way as that of a single crystal, as was done above.

The domain structure of the specimen can influence the character of the ferromagnetic resonance[9]. In all the formulae given above it has been assumed that the specimen is magnetised to saturation, i.e. consits of a *single* ferromagnetic region of arbitrary magnetisation. Indeed, in the majority of ferromagnetic resonance experiments (including studies on catalysts) this condition is satisfied, because very high magnetic fields are used (several thousand Oersted). Allowance for the domain structure is essential in work with weak fields, when saturation magnetisation may not be achieved, leading to non-uniformity of magnetisation and therefore to line broadening and to a shift in the g-factor.

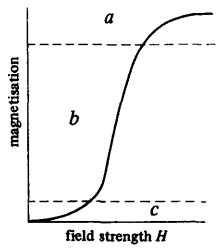


Figure 10. Characteristic magnetisation curve of a ferromagnetic: *a*) rotation processes; *b*) irreversible motion of domain walls; *c*) reversible motion of domain walls.

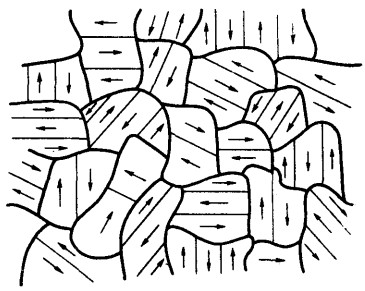


Figure 11. Microstructure of a non-magnetised polycrystalline ferromagnetic.

Let us consider the effect on the magnetic properties of the particles of size significantly less than the domain size. A one-domain particle, like a single crystal, has an axis of easy magnetisation, and the total magnetic moment of the particle in the absence of a field is oriented along the axis of easy magnetisation. Because of the large exchange interactions, the magnetic moments of neighbouring atoms have parallel orientations, and thermal motion cannot destroy the orientation of the resulting magnetic moment in the domain. When the size of the magnetic particles is drastically reduced the situation can be reached when $kT > K_1V$, where K_1 is the anisotropy constant and V is the volume of the particle. In this case the total magnetic moment of the particle will respond to thermal fluctuations, which will be opposed by the external magnetic field. Thus, the behaviour of the total magnetic moment of a small ferromagnetic particle is not unlike that of paramagnetic ions or molecules. Therefore, the temperature dependence of the magnetisation of these particles can be formally described by the Langevin equation (1), with the only difference that in Eqn. (1) μ is the magnetic moment of the paramagnetic ion, atom, or molecule, whereas in the present case μ is the magnetic moment of the particle, equal to $\mu_i n$ where μ_i is the magnetic moment at saturation of the ferromagnetic (0.6 μ_B for Ni) and n is the number of atoms in the particle. In contrast to classical paramagnetic

particles, the magnetic moment of these very small ferromagnetic crystals is thousands of times greater, and therefore Bean[10,11] has proposed the term "superparamagnetism" for this effect in ferromagnetics.

Since the magnetisation of these particles is formally described by the Langevin equation, the size of the particles can be calculated from the results of magnetic measurements. If the thermal energy is much greater than the energy of the interaction between the magnetic moment and the field, i.e. $kT \gg \mu H$, we have

$$\frac{\sigma}{\sigma_0} = \frac{\mu_{Ni} n H}{3kT}.$$

This equation is fully identical to Eqn. (2). If σ/σ_0 and H are known, we can determine $\mu_{Ni}n$, whence n, and therefore also the particle size, can be calculated.

The problem of the particle size determination of finely divided ferromagnetics, and the thermodynamic study of their magnetic properties, have already been discussed in detail[4,5]. We shall briefly consider these questions to arrive at a better understanding of ferromagnetic resonance in systems of small ferromagnetic particles.

Exchange forces, leading to narrower resonance lines, and dipole–dipole (magnetic) forces, leading to line broadening, are present in both paramagnetic and ferromagnetic substances. However, exchange interaction is very much stronger in ferromagnetics than in paramagnetics[12], and therefore quite narrow resonance lines (400–600 Oe) can be obtained with fairly coarse ferromagnetic particles. For iron single crystals lines as narrow as 40–60 Oe are possible. The situation is quite different with "superparamagnetic" particles of 10–15 Å dimensions. As stated above, thermal motion in these particles imposes a fluctuation on the total magnetic moment, the magnetisation of the particles is greatly reduced, and the Curie point is abnormally low[5,13]. All these phenomena arise from the decreased exchange interaction in particles of this type. As a result, resonance lines can become extremely broad and practically undectable (due to dipole–dipole broadening) in catalysts with a low content of ferromagnetic supported on a carrier of large surface area (Ni–SiO_2, Ni–Al_2O_3, etc.) and therefore consisting of small particles. In these cases the ferromagnetic resonance signal can be developed by sintering the catalyst, which increases the particle size of the ferromagnetic.

However, the dependence of the width of the resonance line on the disperseness of the ferromagnetic is a complex problem, and relevant data in the area of catalyst studies are practically non-existent. Some work in this general area has been done on ferromagnetic resonance in thin layers[14]. Fig. 12 shows the effect of the thickness of a Co film on the width of the ferromagnetic resonance line. The steep rise of ΔH at film thicknesses below 500 Å is ascribed to structural non-uniformity of the thin layers, implying non-uniformity of magnetisation and consequent line broadening. However, the results of studies of ferromagnetic resonance in thin layers (Ni, Co, Fe) cannot be directly applied to catalysts of the ferromagnetic metal–carrier type.

There is yet another effect tending to produce non-uniform magnetisation and a broadening of the absorption line in work with metallic ferromagnetics: the so-called "skin effect". This effect arises from the finite (1000–10 000 Å) depth of penetration of a high-frequency field in metals, resulting in non-uniform magnetisation in depth of the crystal. In studies of catalysts this effect can be ignored in most cases, because ferromagnetic crystals on a carrier are usually much smaller than the range of thicknesses quoted above.

The temperature dependence of the width of the ferromagnetic resonance line in ferromagnetic metals is also very interesting. For these materials (and in particular for Ni) ΔH remains practically constant between room temperature and the temperature of liquid helium, and increases steeply on approaching the Curie point[15] (Fig. 13).

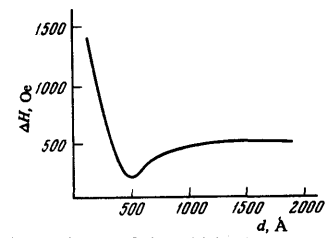


Figure 12. Dependence of the width of the resonance curve on the thickness of thin films of Co.

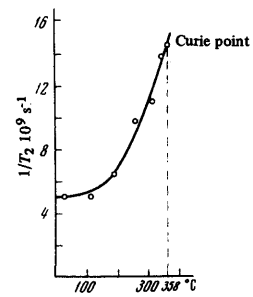


Figure 13. Dependence of relaxation frequency $1/T_2$ (proportional to the line width) on temperature, for Ni.

In this section we have considered various factors which influence the width of the ferromagnetic resonance line and the g-factor. If it were possible to exclude all the effects tending to broaden the distort the absorption curve, one could arrive at the true line width determined only by the relaxation processes in the ferromagnetic. The characterisation of the relaxation processes actually responsible for the width of the true absorption line is a complicated problem which has not yet been fully resolved[16]. An important consideration is the fact that electron–spin relaxation through the conduction electrons in a metal may be the most important of the various relaxation processes available to ferromagnetic metals and capable of giving rise to a resonance line of finite width. If such is the case, it should be possible to change the ferromagnetic resonance conditions and thus attempt to explain, for example, the interaction between metal and carrier, by somehow changing the concentration of conduction electrons in a ferromagnetic crystal whilst keeping constant all the other parameters which influence ΔH.

III. EXPERIMENTAL WORK ON THE APPLICATION OF THE FERROMAGNETIC RESONANCE METHOD TO THE STUDY OF CATALYSTS

1. Study of Hydrogen Chemisorption

Various investigations of the chemisorption of hydrogen on Ni by magnetic methods have been reviewed by Selwood[4]. Magnetic methods can be applied to the study of chemisorption processes only when the ratio of the number of surface atoms to the number of atoms in the bulk is not too small (~ 0.6). This condition is satisfied for Ni crystals of less than 50 Å dimensions, i.e. for crystals which behave magnetically as superparamagnetics.

This size of Ni crystals is necessary also in studies of chemisorption by the ferromagnetic resonance method. The best catalyst from this point of view is Ni supported on SiO_2 or an alumina–silica, because Ni crystals of 10–50 Å size can be produced on these carriers. These were, indeed, the catalysts used by Selwood[17] to study the chemisorption of H_2 by the ferromagnetic resonance method. Catalysts containing 1–50% of Ni were prepared by saturating SiO_2 with a solution of $Ni(NO_3)_2$, followed by drying and reduction at 350°. The hydrogen chemisorbed during the reduction process was pumped off at 350°. The ferromagnetic resonance spectrum was recorded before and after exposure to hydrogen. Catalysts containing 10% Ni were examined in greatest detail: their ferromagnetic resonance spectrum before and after adsorption of hydrogen is reproduced in Fig. 14. The line width is unaffected (within experimental

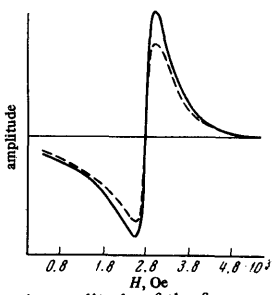


Figure 14. Change in amplitude of the ferromagnetic resonance line during adsorption of H_2 on Ni-SiO_2.[17] Continuous line—before adsorption; dashed line—after adsorption.

error) by the exposure to hydrogen, and remains at 470 ± 30 Oe, but the amplitude of the signal decreases by 15–25%. The g-factor, equal to 2.22, is also unaffected by the admission of hydrogen. As expected, the decrease in amplitude was a function of the particle size of the Ni. Thus, with a commerical catalyst of average Ni particle size 40 Å the decrease in amplitude was only 6%, and for the catalyst described above containing 10% Ni and having an average Ni particle size of 15 Å the decrease in amplitude was ~18%. Selwood showed that the decrease in amplitude was linearly related to the amount of hydrogen chemisorbed. Thus, the ferromagnetic resonance method qualitatively confirms the results obtained by static or low-frequency magnetic methods. However, Selwood points out that the main advantage of the ferromagnetic resonance method as compared with other magnetic methods is its very high sensitivity. He assumed that very small Ni crystals can be obtained by using catalysts with a low Ni content, and that these crystals will contain an extremely large number of surface Ni atoms, thus giving an enhanced change in the intensity of the ferromagnetic resonance signal.

Unfortunately, the sensitivity of the ferromagnetic resonance method is not such a simple problem. For measurements on catalysts containing relatively coarse Ni particles (>200 Å), the ferromagnetic resonance method offers no advantage over static magnetic methods of measuring the amount of ferromagnetic phase. If the concentration of Ni on the surface is decreased at the same time as the particle size, the sensitivity of the ferromagnetic resonance method does not increase, but actually decreases. We have already pointed out that low concentrations of small Ni particles on the surface produce a drastic broadening of the ferromagnetic resonance line due to the effect of dipole–dipole interaction. This substantial line broadening associated with low Ni concentrations on the carrier has in fact been observed in studies of Ni catalysts on charcoal[18]; the effect results in a loss of sensitivity, and imposes a limit on the application of the method to systems of this type. Furthermore, very small amounts of material (0.1–10 mg) are used for plotting ferromagnetic resonance spectra: quantitative adsorption data cannot be obtained under these conditions. Hence, there is no justification at the moment for the belief that the ferromagnetic resonance method is more sensitive in hydrogen chemisorption studies than the low-frequency permeameter method, which can accept large amounts of material (up to 10 g) and has an acceptable sensitivity. The real advantage of the ferromagnetic resonance method over other magnetic methods is the potential access to new information, in principle, on the structure and properties of Ni in catalysts, information which cannot be obtained by other methods.

A paper by Loy and Noddings[19] also describes a study of the interaction between Ni and hydrogen. These workers investigated the catalyst $NiCa_8(PO_4)_6$, used in the dehydrogenation of butene to butadiene. The interaction between hydrogen and the catalyst was analysed in two ways: 1) from the dependence of the amplitude of the ferromagnetic resonance signal upon the temperature of exposure of the catalyst to hydrogen, and 2) by saturation of the Ni with hydrogen at high temperatures, followed by desorption of the hydrogen at the same temperature.

The first method involved the following experimental procedure. The catalyst pellet was reduced for 15 min at the desired temperature, and the ferromagnetic resonance spectrum was recorded at room temperature. The specimen was next oxidised at the reduction temperature and the spectrum was again recorded. This oxidation–reduction cycle was repeated on the same pellet over the temperature range 400–800°.

In the second method the catalyst was reduced in a stream of hydrogen at 1100° for 30 min, the ferromagnetic resonance spectrum was measured, the hydrogen was pumped off at 1100° for 1.5 h, and the spectrum was again measured.

Fig. 15*a* shows the ferromagnetic resonance spectrum after an oxidation–reduction cycle by the first method. The line width for the reduced catalyst is 720 Oe, and $g = 2.2$. No signal is obtained after oxidation. The change in the relative intensity of the ferromagnetic resonance signal as a function of the temperature of hydrogen treatment is shown in Fig. 16. The authors interpret this behaviour by postulating the occurrence of two processes.

1. Catalysts reduced below 670° contain metallic Ni, produced by the reduction of Ni^{2+}, in an amount which increases with increase of reduction temperature, accompanied by a corresponding increase in the intensity of the ferromagnetic resonance signal.

2. Reduction of the catalyst above 670° leads to a decrease in signal intensity, due to the decreased magnetisation of the Ni following hydride formation in the bulk or on the surface of the Ni crystals.

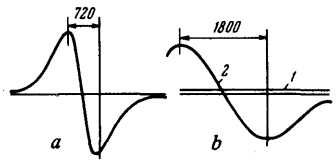


Figure 15. Resonance absorption curve for a nickel–calcium phosphate catalyst:
a) reduced at 680°; *b*) reduced at 1100° (*1*) and degassed at 1100° (*2*).

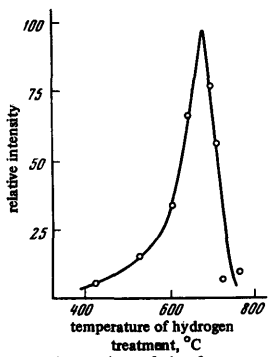


Figure 16. Relative intensity of the ferromagnetic resonance signal of a nickel–calcium phosphate catalyst as a function of the temperature of reduction.

Fig. 15*b* shows the ferromagnetic resonance spectra of a catalyst reduced at 1100° and degassed at 1100°. The reduced catalyst does not give a signal, but the outgassed catalyst gives a broad line ($\Delta H = 1800$ Oe) with $g = 2.55$. The authors suggest that reduction at 1100°C produces the diamagnetic nickel hydride, which is decomposed by evacuation at 1100° with regeneration of metallic nickel, which gives a ferromagnetic resonance signal. Thus, the conditions for the interaction of Ni with hydrogen chosen in this work are quite different from those of Selwood's work, in which hydrogen chemisorption was studied. Obviously, in Loy and Noddings' work nickel hydrides are formed, i.e. there is formation of bulk chemical compounds. Furthermore, at the high heat treatment temperatures used in this work sintering of the metallic nickel must be substantial, and yet the authors ignore this process in their subsequent discussion (analysed below).

2. Study of the Shape of Nickel Particles and of the Structure of Nickel Catalysts

The earliest application of the ferromagnetic resonance method was in a study of the structure of nickel catalysts prepared by the decomposition of Ni formate in sunflower oil in a stream of hydrogen[20]. X-Ray diffraction and magnetic studies of the catalysts were used to complement the ferromagnetic resonance spectra. It was shown that the *g*-factor calculated without applying corrections for the crystallographic magnetic anisotropy and for shape anisotropy was 2.22, i.e. the particles were spherical. In contrast to the behaviour of Raney nickel catalysts,[21] dehydrogenation does not increase the magnetisation and the intensity of the ferromagnetic resonance signal: on the contrary, it is accompanied by fragmentation (the particle size falling from 100 to 50 Å) and by a decrease in magnetisation (from 7.2 to 0.30). The dehydrogenated catalyst has a very labile structure consisting of finely divided Ni (width of the ferromagnetic resonance line 300 Oe), which undergoes extensive sintering at moderate temperatures.

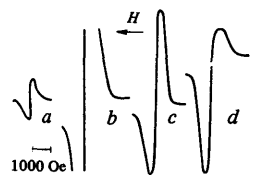


Figure 17. Ferromagnetic resonance spectra of heat treated nickel formate catalysts:
a) starting catalyst; *b*) catalyst sintered in air for 2 h at 300° (at the same amplification); *c*) catalyst sintered in vacuum for 4 h at 300°; *d*) catalyst sintered in air for 4 h at 300°C.

Fig. 17 shows the ferromagnetic resonance spectra of the formate catalyst, dehydrogenated by nitrobenzene, for various conditions of heat treatment. It is evident that sintering the catalyst in air at 300° (Fig. 17*b*) produces a sharp increase in the intensity of the signal. This is due to the fact that with a very labile and "loose" catalyst structure the growth of Ni particles, accompanied by an increase in magnetisation, is much faster than the oxidation of Ni to NiO. Typically, sintering the catalyst in a vacuum or in the air causes substantial line broadening (from 300 to 900 Oe), increase of particle size (from 50 to 200 Å), and increase of magnetisation (from 0.3 to 14.0), but sintering in the air additionally gives a sharply asymmetric line (Fig. 17*d*). As stated above, these processes are determined by non-uniform magnetisation of the sample (due to magnetic anisotropy, shape anisotropy, NiO impurities), which increases with increase of the Ni particle size.

Gasumura and Abe[22] have reported a study of the ferromagnetic resonance spectra of two Raney nickel catalysts, prepared by leaching a melt containing 49% Ni and vacuum heat treatment (10^{-3} mmHg) for 2 h at 70° and 300°. The catalyst prepared at 70° was active towards hydrogenation and had a magnetisation of 11.0; that treated at 300° was inactive with a magnetisation of 27.0. The ferromagnetic resonance spectra of both catalysts are shown in Figs. 18*a* and 18*b*. The line asymmetry of the catalyst heated at 70° is not due to anisotropy of the *g*-factor, as stated by the authors, but to shape anisotropy (see Fig. 7) or to magnetic

anisotropy. The question can be resolved by measuring the temperature dependence of the asymmetry coefficient of the line. In this case the asymmetry of the line is evidently associated with shape anisotropy, since sintering of the catalyst gives a symmetrical line with $g = 2.22$ (Fig. 18*b*). The increased magnetisation on sintering is due mainly to growth of the Ni particles, and not to the evolution of hydrogen. The lower catalytic activity of the catalyst heated at 300° evidently has the same explanation.

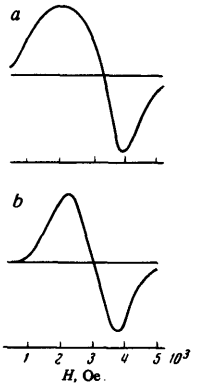


Figure 18. Ferromagnetic resonance spectra of Raney nickel catalysts[22]:
a) catalyst heated in vacuum at 70°C, $g = 2.09$; *b*) catalyst heated in vacuum at 300°C, $g = 2.22$.

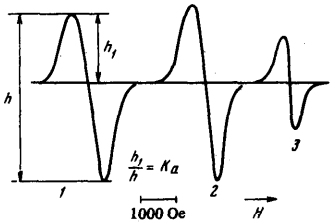


Figure 19. Temperature variation of the asymmetry coefficient (K_a) of the line for Ni–ZnO catalysts (49.5% Ni):
1) 20°; *2*) 100°; *3*) 220°C.

A similar increase in the symmetry of the line with a tendency of the *g*-factor towards the value 2.20 (characteristic of spherical particles), and increased magnetisation, was observed during the sintering of Ni prepared by chemical reduction with sodium hypophosphite[23]. A study has been reported[24] of the temperature dependence of the asymmetry coefficient of the ferromagnetic resonance line for Ni–ZnO catalysts. The results are given in Table 1 and Fig. 19. It can be seen that the line becomes more symmetrical as the measurement temperature is raised. Thus, the asymmetry of the ferromagnetic resonance line in this case is not due to shape anisotropy of the particles (since there is no sintering of the catalyst during the measurements) but to a steep temperature dependence of the Ni anisotropy constant (see Fig. 4), and hence to a decreased non-uniformity of magnetisation at higher measurement temperatures. It is obvious, therefore, that the existence of line asymmetry can be interpreted only as an indication

Table 1. Variation of the asymmetry coefficient of the ferromagnetic resonance line (K_a) with measurement temperature

Concentration of Ni, wt.%*	Catalysts reduced from oxides**					Concentration of Ni, wt.%	Catalysts reduced from hydroxides***				
	temperature dependence of K_a				*g*-factor		temperature dependence of K_a				*g*-factor
	20°	100°	220°	−196°			20°	120°	210°	−196°	
5.6	0.50	0.50	0.50	—	2.18	5.6	0.50	0.50	0.50	0.43	2.20
8.8	0.45	0.48	0.53	0.04	2.20	9.1	0.5	0.5	0.5	0.30	2.18
14.3	0.46	0.52	0.53	0.01	2.20	20.3	0.47	0.48	0.49	0.16	2.18
39.8	0.36	0.45	0.52	0.13	2.18	56.9	0.54	0.54	0.50	0.11	2.30
49.5	0.41	0.44	0.49	—	2.18	66.8	0.46	—	—	—	—
51.0	0.26	0.41	0.50	—	2.20	81.8	0.34	0.44	0.44	0.05	2.30
77.3	0.31	0.48	0.49	0.01	2.54	91.8	0.18	0.48	0.53	—	3.00

* Concentration of Ni quoted with allowance for partial reduction.
** Prepared by reduction from NiO–ZnO samples heated at 600°C.
*** Prepared by reduction from the hydroxides $Ni(OH)_2$–$Zn(OH)_2$ dried at 100°C.

of the presence of non-uniform magnetisation, but not of the origin of the non-uniformity. The underlying causes can only be established by a detailed study of the specimen using different methods, and in particular by observing the temperature variation of the shape of the ferromagnetic resonance line.

3. Interaction Between Ni Particles in Catalysts According to Ferromagnetic Resonance Data

The problem of the interactions within Ni particles and between particles was formulated on the basis of ferromagnetic resonance data by Loy and Noddings[19]. These workers measured the temperature dependence of the amplitude of the ferromagnetic resonance signal, and obtained the results summarised in Fig. 20. A curve of this

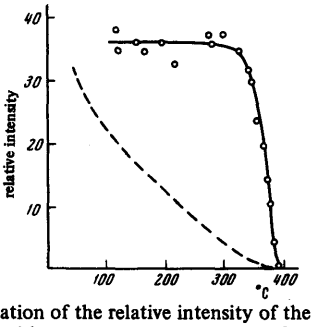


Figure 20. Variation of the relative intensity of the ferromagnetic resonance signal with measurement temperature for a nickel–calcium phosphate catalyst[19]. The dashed curve shows the shape of the thermomagnetic curve for finely divided nickel.

shape for the change in magnetisation with temperature is characteristic of coarsely divided Ni, but the authors state that coarse Ni particles could not have been present in their catalysts because the magnetisation disappears completely under the appropriate conditions in the presence of hydrogen, indicating[17] that the Ni particles must be very finely divided. But finely divided Ni particles should have a low Curie point (not 358°, as suggested by Fig. 20), and their thermomagnetic curve should have the shape of the dashed line in Fig. 20. Loy and Noddings explain these

anomalies by postulating that resonance methods measure transitions in individual domains, whereas static measurements encompass the whole particle including inter-domain interactions. In small particles this interaction is distorted by thermal energy, leading to abnormally low Curie points. The authors consider that the particle size and the influence of thermal vibrations are reflected only by the line width, and not by the Curie point. However, this explanation seems to be physically unsound for the following reasons.

1. There is not justification at all for associating the loss of magnetisation on exposing the catalyst to hydrogen at temperatures as high as 800–1100° with the presence of small particles. At those temperatures the interaction of hydrogen with nickel ceases to be a surface chemisorption effect, and involves the whole mass of the particle in formation of a bulk hydride phase, as the authors themselves point out. Obviously, as soon as the loss of magnetisation can be ascribed to the formation of a bulk phase of nickel hydride, it is no longer necessary to consider only very small nickel particles, and the same process can occur with coarse nickel crystals.

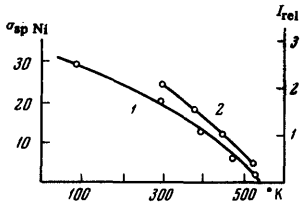


Figure 21. Temperature dependence of the saturation magnetisation (*1*) and of the relative intensity of the ferromagnetic resonance signal (*2*) for a Ni–ZnO catalyst (20.3% Ni).

2. With very small Ni crystals—complete demagnetisation under the influence of hydrogen is theoretically possible for a particle size < 10 Å—the concept of domains and domain boundaries (see Section II,4) loses physical significance, because such particles are not subdivided into domains. Therefore, the suggestion that in these particles the transitions within domains are characterised by resonance methods whilst static methods include interactions between domains is not physically justified. Both static and resonance methods should give the same type of change of magnetisation with temperature. This was actually demonstrated by the present writer[24] for an Ni–ZnO catalyst. Curve *1* of Fig. 21 was obtained from static measurements, and curve *2* shows the relative change of the integral intensity of the ferromagnetic resonance signal. It is evident that the two curves have entirely similar trends, i.e. that the presence of fine Ni particles in the catalyst is manifest in both static and resonance methods. The influence of various factors on the line width has already been treated in detail in previous Sections. Measurements on a single catalyst at a single temperature usually provide very little information on the underlying causes of the observed line width.

Data on the temperature dependence of the line width for a series of Ni–ZnO catalysts are set out in Table 2. All the catalysts show a characteristic decrease in line width with increase of temperature, and an increased line symmetry (Table 1). It follows that additional line broadening is due to magnetic crystallographic anisotropy rather than to shape anisotropy of the particles. The higher the measurement temperature, the lower is the magnetic anisotropy constant (see Fig. 4), and the less substantial is the line broadening due to this factor. As already pointed out above, from the point of view of magnetic anisotropy the line width is relatively insensitive to temperature until it begins to rise steeply on approaching the Curie point. Therefore, the opposite change of ΔH with temperature for Ni–ZnO catalysts must be ascribed to magnetic crystallographic anisotropy, and this effect should not be ignored in work with powdered materials.

Table 2. Variation of the width (ΔH) of the ferromagnetic resonance line with measurement temperature.

Concn. of Ni, wt.%, allowing for incomplete reduction	Catalyst reduced from oxides				
	temperature dependence of ΔH, Oe				ΔH, Oe after sintering*
	20°	100°	220°	−196°	
5.6	780	690	660	—	1700
8.8	780	720	660	1170	1320
14.3	750	660	660	1260	960
39.8	1050	780	660	1620	1350
49.5	1600	1250	680	1740	1800
51.0	1440	1080	690	3500	1860
77.3	2340	2040	1380	—	—

* Sintering in vacuum (10^{-5} mmHg) for 12 h at 410°C.

Since the line width measured at 220° is practically constant in catalysts containing 5.6–51% Ni (Table 2), the width is evidently determined by strong exchange interactions within the particles (particle size 400 Å) and relatively weak interactions between particles. Sintering of the catalysts causes increased magnetisation, growth of the Ni particles, and therefore also a greater influence of the anisotropy effect ($K_1 V \gg kT$) and considerable line broadening (Table 2). Simultaneously decreasing the size of the Ni particles on the carrier and their concentration produces considerable line broadening[18], obviously through dipole–dipole interaction. However, in the presence of a large number of fine Ni particles very close to each other the state of affairs can be quite different. Thus, with Ni particles prepared by decomposition of nickel formate in oil and having dimensions of the order of 40 Å, the line width was found[20] to be only 300 Oe. This value is even lower than the value reported[25] for colloidal Ni particles. Obviously, with high densities of small ferromagnetic particles in close proximity the dipole–dipole broadening is masked by the exchange interactions which tend to sharpen the line. Characteristically, the line width for this catalyst does not change on going to −196°, i.e. it is not determined by spin–lattice relaxation and magnetic anisotropy: it may be close to the true line width characteristic of the material.

Ni–Al_2O_3 catalysts have been investigated by Rubinshtein and coworkers[26]. Even small (5 wt.%) additions of Al_2O_3 enable a symmetrical ferromagnetic resonance signal to be observed ($g = 2.2$, $\Delta H = 1400$ Oe). Pure Ni under the same reduction conditions (350°C) gives a line so broad as to be almost impossible to plot (Figs. 22*a* and 22*b*). Reduction of the same catalyst at 450°C produces some line broadening ($\Delta H = 1550$ Oe) and above all an increase of the *g*-factor to 2.8. This is due to slight sintering of the Ni crystals, and to the associated increase in the non-uniformity of magnetisation, leading to line broadening

and a change in the g-factor. The effect is entirely analogous to the result obtained[19] for a nickel–calcium phosphate catalyst reduced at 1100°, and is further confirmation of the sintering processes which Ni undergoes at these temperatures. The major effect of small additions of Al_2O_3 on the ferromagnetic resonance spectrum of Ni is explained by a substantial increase in the disperseness of the nickel (60–100 Å). The structure of the catalyst may be depicted as Ni particles (60–100 Å in size) separated by thin layers of Al_2O_3. This structure is very stable towards sintering and very resistant to oxidation because of the slow diffusion of O_2 to the Ni particles, as shown by Rubinshtein and coworkers[26].

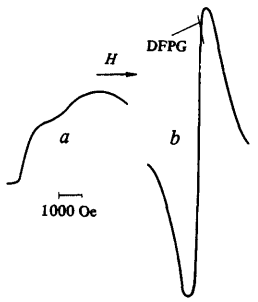


Figure 22. Ferromagnetic resonance lines for Ni and Ni–Al_2O_3 catalysts:
a) pure Ni; *b*) Ni–Al_2O_3 (~5% Al_2O_3).

We shall now briefly discuss the determination of the concentration of Ni, and its magnetisation, from ferromagnetic resonance data. Loy and Noddings[19] have computed the number of Ni atoms and the approximate domain size by comparing the area under the ferromagnetic resonance curve with the area under the curve of a *paramagnetic standard* ($MnSO_4.H_2O$). This procedure is, of course, physically quite unsatisfactory for quantitative calculations, because a ferromagnetic with the same number of atoms as a paramagnetic is subject to exchange forces giving rise to enormously greater values of the magnetisation. Even more unsatisfactory is the method proposed by Fasman[27], in which the relative integral intensities of ferromagnetic resonance lines are calculated by the formula $I = A(\Delta H)^2$, where A is the amplitude of the second derivative and ΔH is the line width. This formula is analysed, and the conditions under which it can be applied are discussed, in Refs. 6 and 28. It is used to calculate the concentration of unpaired spins in paramagnetic materials, by reference to a standard, in the case of *symmetrical lines*. For asymmetric lines the use of this formula is inadmissible, because it leads to considerable errors. The saturation magnetisation has been evaluated from ferromagnetic resonance data[9] by means of the formula

$$\mu''_{res}\,\Delta H = 4\pi\sigma_0$$

where μ''_{res} is the imaginary part of the dynamic permeability under resonance conditions, ΔH is the line width, and σ_0 is the saturation magnetisation of the sample.

Calculation of the change in relative intensity requires a double integration of the absorption line (when plotted in the form of the first derivative), followed by measurement of the area under the curve, which is proportional to the magnetisation.

As regards the quantitative determination of Ni in the catalysts, the problem is very much complicated by the fact that for a given number of Ni atoms in the sample the magnetisation (or area under the absorption curve) will be strongly dependent on the size of the particles formed by the Ni atoms. Therefore, each catalyst sample requires its own standard with the same size distribution of Ni particles. It is very difficult, of course, to fulfil this condition.

4. Interaction of the Metal with the Carrier

In recent years, the study of the structure and of the catalytic activity of supported metal catalysts has attracted increasing interest, and the problem has become a key one in catalysis. An important aspect of this problem is whether direct electronic interaction is present between the carrier and the metal, and whether the catalytic activity is thereby affected. Various workers have shown[29–32] that doping of the carriers (Al_2O_3, ZnO, MgO) with different cations (Li^+, Ga^{3+}) which affect their electrical conductivity produced a change in the catalytic activity of the deposited nickel. We shall not attempt a detailed analysis of these researches, and we shall consider only the physical effect which underlies these observations.

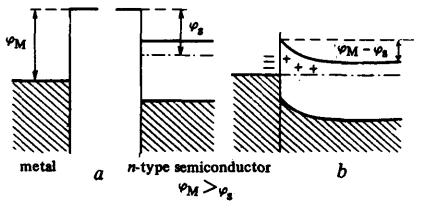


Figure 23. Energy level diagram for the contact between a metal and an n-type semiconductor:
a) before contact; *b*) after contact.

The physical effect is based on phenomena at the metal–semiconductor interface. Assume an n-type semiconductor of work function φ_s and a metal of work function φ_M, such that $\varphi_M > \varphi_s$ (see Fig. 23*a*). If the metal is brought into contact with the semiconductor, electrons from the semiconductor (at a higher chemical potential) will be transferred to the metal until the chemical potentials in the metal and the semiconductor are equal. As a result, the layer of semiconductor adjacent to the metal becomes depleted of current carriers and positively charged, and the metal layer becomes negatively charged. At the boundary, a potential barrier is formed (Fig. 23*b*): this barrier plays an essential role in rectifying contacts. An analogous model can be set up for the case of a metal deposited on a p-type semiconductor. This transfer of electrons to the metal from the semiconductor (metal–n-type semiconductor boundary, $\varphi_M > \varphi_s$) or to the semiconductor from the metal (metal–p-type semiconductor boundary, $\varphi_M < \varphi_s$) is invoked by the authors of these papers to account for the change in catalytic activity of the Ni deposited on variously doped

carriers. And yet, the reality of this transfer in catalysts has not so far been demonstrated. Can the ferromagnetic resonance method be applied to the solution of this problem? We have already pointed out that the true line width is determined by the interaction between the ferromagnetic system of electrons and the conduction electrons. Hence, if the metal is depleted or enriched of electrons, the relaxation time (and therefore also the line width) can be expected to change. Thus, the experiment consists in determining changes in line width for Ni deposited on carriers having different electrical properties. However, such an experiment is very difficult to realise, because (as stated above) the line width in systems of the catalyst type is not determined exclusively by relaxation processes. The experiment requires that the Ni on the various carriers should have: 1) an identical size distribution of Ni particles; 2) identical particle shape, so as to exclude shape anisotropy; 3) identical and preferably low concentration of Ni on the carrier, so as to avoid interaction between Ni particles.

The measurements should be made at high temperatures, in order to avoid line broadening through magnetic crystallographic anisotropy. The Ni particles should have the greatest possible degree of disperseness, but such as to allow resonance to be observed, since the effect will be most pronounced in this case. Of course, it will not be easy to fulfil all these conditions, but qualitatively new information on the structure of metallic catalysts on carriers can be expected from work of this type.

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The ferromagnetic resonance method has recently begun to be applied to the study of ferromagnetic catalysts in parallel with the various magnetic methods of investigating paramagnetic and ferromagnetic catalysts. The method is capable in principle of producing qualitatively new information on the properties of ferromagnetic catalysts, which cannot readily be obtained by other methods: 1) on the interactions within and between ferromagnetic particles; 2) on the structure of ferromagnetic catalysts and its dependence on various influences; 3) on the interaction between the catalyst and various adsorbents; 4) on the shape of the ferromagnetic particles; 5) on the nature of the interaction between the ferromagnetic metal and the carrier.

We may hope that extensive application of this method will result in an even closer approach to an understanding of the structure of real catalysts and to the development of a modern theory of catalysis.

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