

Developments in Magnetism Since the Second World War

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1 Introduction

I was given this task by Allan Mackintosh. Against his unique combination of charm, wit, and determination it was impossible to refuse. Only later when I realised the size of the task did I begin to wonder why his choice had fallen on me. In looking back I found that Casimir had expressed my sentiments precisely at the beginning of a talk he had given 20 years ago. He said “as a young physicist I regarded an interest in the history of physics as an unmistakable sign of either incompetence or beginning senility. Today I am inclined to regard a lack of interest in the history of our science as a mark of deplorable immaturity”. But, perhaps unfairly, I began to suspect that Allan had some deeper motive. As we all know his tremendous curiosity and energy had recently led him to take an interest in, and write articles about, some aspects of the history of science. I believe that Allan had something special he wanted to tell us about the development of magnetism, and I was the straw man who was introduced to set the scene.

Alas, we shall never know what Allan had in mind. You are left with only my dry bread for the sandwich and the spicy filling that he would have provided is missing. Such feelings of loss spread far beyond the subject of this talk. For 30 years I have talked physics with him, and together we have watched and contributed to the development of our understanding of the rare earths. In recent years, because of other distractions, these meetings have been less frequent but he remained a good friend – one of the few people of whom one could honestly say that you were really pleased to see him whatever the circumstances. All our lives, and our subject, have been made irretrievably the poorer by his death.

2 Background

Turning to the subject it was necessary to find some definition which would restrict the topic to manageable proportions. I decided to define "Magnetism" as the material covered in the regular International Conferences on Magnetism which have been held every 3 years since Grenoble in 1958 to the 13th of the series in Warsaw in 1994. The proceedings of these meetings are listed in the References (Proc. I.C.M., 1959, 1962, 1964, 1968, 1971, 1974, 1977, 1980, 1983, 1986, 1988, 1992, 1995). Although not technically part of the sequence there were two earlier meetings with a similar format in 1950 also in Grenoble (Colloque Int. de Ferro et Antiferromagnetisme, 1951) and in 1952 in Maryland (Magnetism Conference, 1953). These were landmarks in the development of the subject because the changes brought by the war, both in new techniques like magnetic resonance and neutron diffraction, and also in the greatly increased support for research in this area, were already being felt. These changes can be thrown into sharp relief by comparison with the only other major international conference of this type ever held, that in Strasbourg in May 1939 (Le Magnetisme, 1940).

To be complete there had been one other major international conference devoted to Magnetism at an earlier date, the Solvay Meeting of 1930 (Le Magnetisme, 1932), but I do not think we ordinary mortals would have recognised it as such, although I believe we would have been at home in all the later meetings. Only about a dozen papers were presented to the Solvay Conference but the roll-call of participants sounds more like that for a scientists Valhalla. It included Bohr and Einstein, Heisenberg and Dirac, Sommerfeld and Pauli, Fermi and Kapitza as well as Langevin, Weiss, Zeeman and van Vleck. The actual papers seem much more prosaic. It is hard for us to understand the enormous leaps of comprehension which were necessary to apply the new quantum mechanics. But after its dramatic success in atomic physics, magnetism proved one of the most fruitful areas of applicability. van Vleck's book "The Theory of Electric and Magnetic Susceptibilities" (van Vleck, 1932) and Stoner's "Magnetism and Matter" (Stoner, 1934) remain classics to this day.

In 1939 the fundamental ideas which underpin our understanding of magnetic phenomena today were largely in place. The Strasbourg conference of that year was able to look back also to the triumphs of the classical era. Weiss was its Chairman and although Langevin was too ill to attend his comments on the development of magnetism during the preceding 50 years were included in the paper by his colleague Bauer. Langevin's work at the turn of the century (Langevin, 1905) on diamagnetism and paramagnetism, and his derivation of the famous formula of the magnetisation of an assembly of classical magnetic dipoles had, together with Curie's empirical law (Curie, 1895) for the susceptibility, proved a significant

milestone in our understanding of magnetic materials. Weiss' brilliant concept of the molecular field not only provided a basic understanding of ferromagnetism but gave us a prototype theory for all phase transitions. In spite of red herrings like the existence of a fundamental (Weiss) magneton, quantum mechanics now provided a sound basis for the explanation of these phenomena while at the same time removing many of the difficulties which had become apparent in the detailed application of classical theory, particularly to magneto-optic effects.

One of the most bizarre of these was Miss van Leeuwen's theorem (van Leeuwen, 1921) which demonstrated that in classical statistical mechanics the magnetic susceptibility must be zero. (Bohr in his 1911 dissertation had already gone some way towards a similar result). The reason why Langevin's formula violated this theorem, while giving the physically correct result, lay in his assumptions about fixed magnetic dipole moments which were at variance with the strictly classical conditions.

In 1939 several papers were presented giving detailed properties of paramagnetic salts using both static and optical measurements while Simon and Casimir discussed their use in adiabatic demagnetisation. Néel gave a paper on antiferromagnetism and there were references to other types of magnetic order. Kramers discussed both crystal fields and exchange for magnetic ions in insulators. The difficulty in understanding the most important of all magnetic materials, ferromagnetic iron remained much to the fore and Mott's paper on "Recent Progress and Difficulties in the Electron Theory of Metals" was a prototype of many more to come.

Two articles discussing the history of the development of magnetism have appeared in recent years as part of the International Project on the History of Solid State Physics (Keith and Quédec, 1992) and in the Institute of Physics comprehensive history of 20th Century Physics (Stevens, 1996).

3 Post-war growth

At the first post-war conference in Grenoble in 1950 there were 49 contributed papers and by the first ICM in that City in 1958 the number had grown to 78. The next time ICM met in Grenoble in 1970 the number was approaching 500; it passed a thousand in Paris in 1988 and was almost 2000 in Warsaw in 1994. The growth shown in Fig. 1 is not quite exponential but is highly non-linear. At various times there have been attempts to analyse the growth of different aspects of the subject. Figs. 2 and 3 show the distribution between nine rather arbitrary groups of topics made in 1979 and 1985. It is in practice rather difficult to define meaningful categories and to allocate all papers between them.

The rise and fall of some topics is clearly shown, but others are hidden within

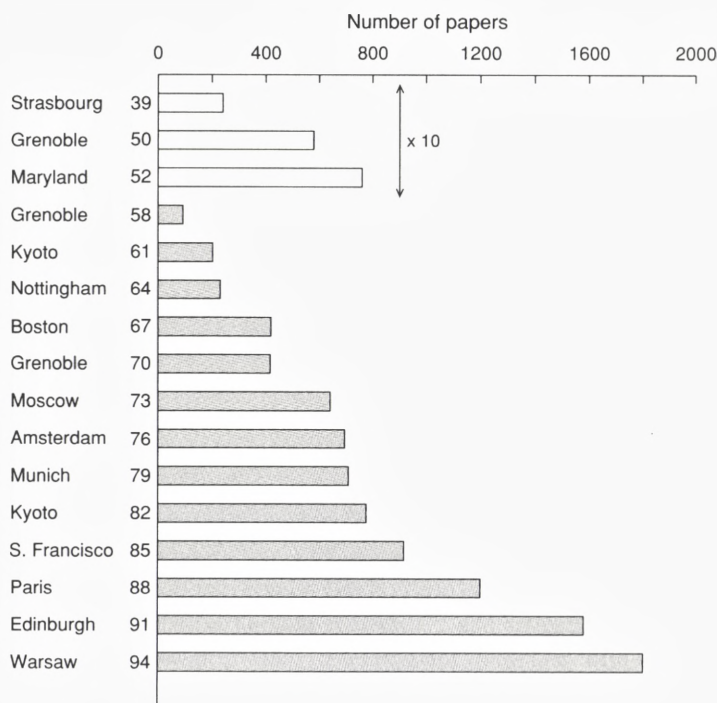


Figure 1. Numbers of published papers at the International Conferences on Magnetism – together with three earlier meetings. The latter are on an enhanced ($\times 10$) scale.

their broader allocation. Perhaps the most dramatic is the rise in interest in disordered spin systems in the 1970's. Until that time, apart from metallic alloying, efforts had concentrated on studying systems which were as pure and regular as possible. This new upsurge of research was partly driven by widespread interest in the newly defined concept of a spin glass. A similar rise in research into phase transitions and in particular into critical phenomena also occurred across this period as improved theories using the renormalisation group, and much more accurate experiments became possible. On the other hand the upsurge of interest in mixed valent and heavy fermion systems, or the impact of new techniques like the Mössbauer effect are less obvious in the numbers.

Throughout the period practical uses of magnetic materials have, of course, attracted the attention of the research community. The improved understanding of magnetic domains extensively described by Bozorth (Bozorth, 1951, see also Colloque Int. de Ferro et Antiferromagnetisme, 1951) has allowed great improve-

ment in the performance of permanent magnets for electric motors, generators, loudspeakers, etc., and of soft magnetic materials for transformers and inductors. In addition the technology of tape recording has been dramatically improved although the basic principles remain unchanged. Attempts to use magnetic materials for data storage has, however, largely lost out to semiconductor materials so that the study of ferrites and garnets which was such an important feature in the 50's and 60's has been attenuated after that period. As a result of these fluctuating fortunes for industrial application the proportion of papers submitted to ICM from industrial laboratories has reduced over the years.

It is almost impossible to know where to start to summarise all this effort. Since this is a conference about Magnetism in Metals I should certainly give that area attention, although it was not in my brief to confine myself to that field. I therefore propose to discuss first the development of our understanding of magnetic insulators, in order to highlight the differences between them and the metals. After that I shall pass to metallic systems with particular reference to the transition metals and finally to the rare earths. I make no apology for emphasising the latter since their properties reflect both those of insulators and metals, of localised and itinerant electrons. They also provide a thread of my own Odyssey through these years – I attended many of the ICM Meetings starting with Maryland in 1952 where I went as a newly graduated D.Phil on my way to a post-doc in Berkeley with Kittel, but they also provide a thread for my longstanding contacts with Allan Mackintosh who was also to be found at these meetings from 1964 onwards. I met him in Warsaw in 1994 and know he was planning to attend the meeting in 1997. His book with Jens Jensen “Rare Earth Magnetism: Structures and Excitations” (Jensen and Mackintosh, 1991) summarises much of our knowledge of the Rare Earths which has been accumulated since the war.

4 Insulators

As has been said the basic properties of the insulating salts of the $3d$ transition metals and the rare earths were broadly understood by the beginning of the period under review, and similar compounds from the $4d$ and $5d$ series, together with the actinides, could also be accounted for by extensions of the basic model. In its simplest form this regarded the transition metal ion as an isolated entity interacting with its surroundings only by a crystalline electric field derived from the Coulomb forces of the charges on the surrounding ions. In the case of the rare earths the $4f$ electrons lay inside the outer shells and hence experienced only a weak field. As a result their magnetic properties closely resembled those of the free ions, although significant changes were observed at low temperatures due to the splitting of the

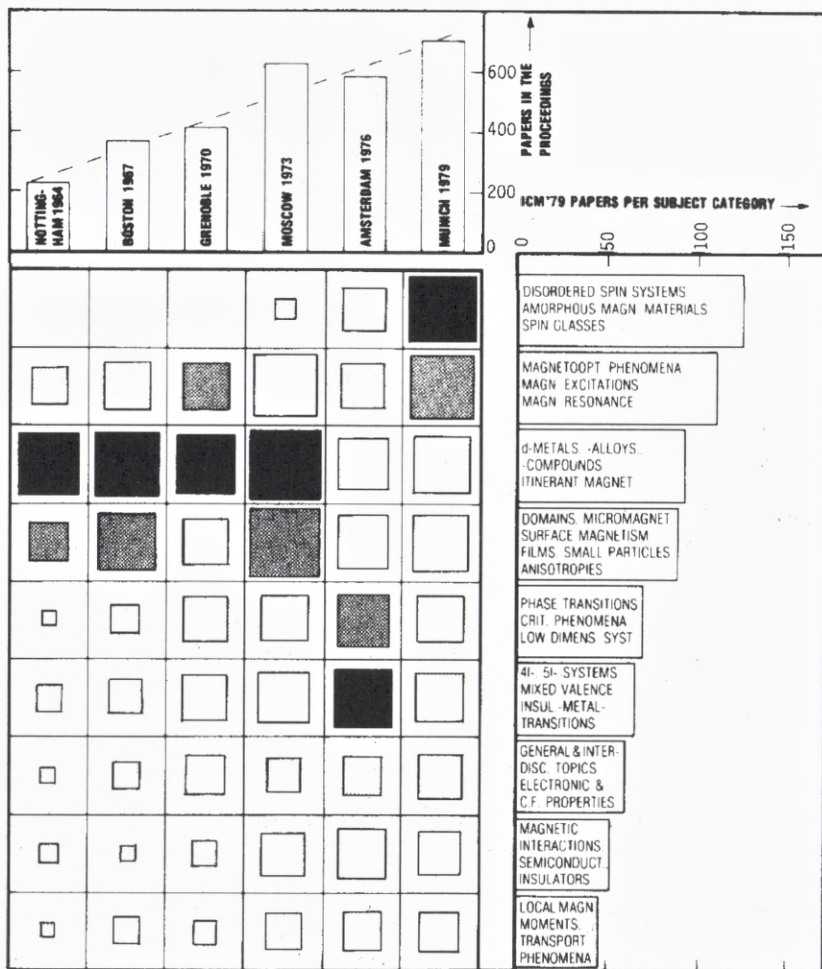


Figure 2. Distribution of papers at various ICMs in various categories (after Proc. I.C.M., 1980).

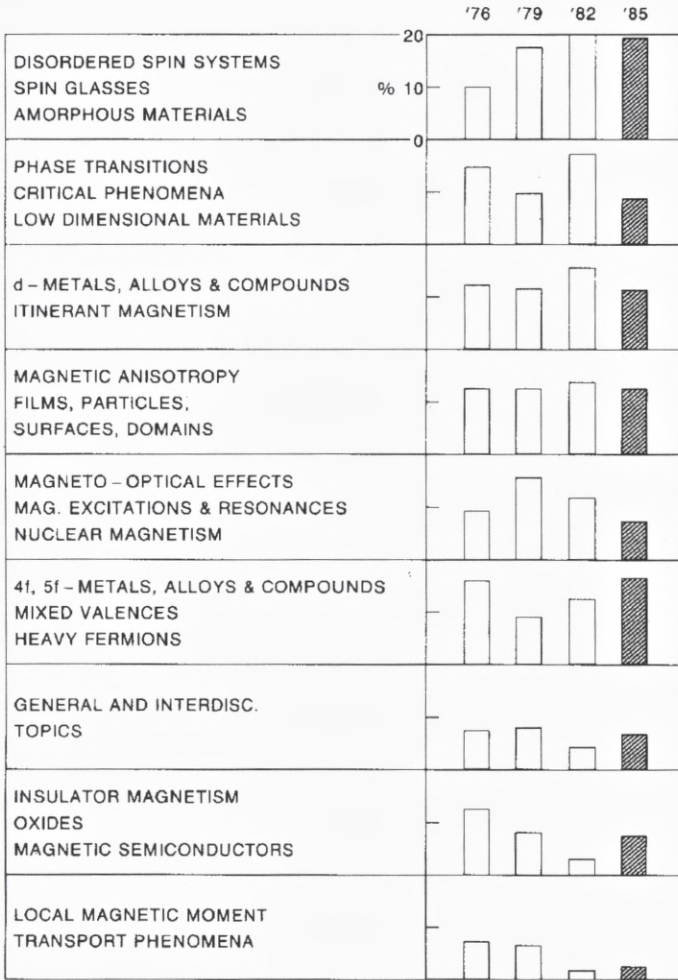


Figure 3. Distribution of papers at various ICMs in various categories (after Proc. I.C.M., 1986).

spin-orbit multiplets with total angular momentum J by the field. However, the salts of the transition metals usually exhibited a spin-only magnetic moment. Here, the larger crystalline field was believed to split the energy levels of the lowest Russell-Saunders multiplet so that the degeneracy arising from the total angular momentum L was removed while the degeneracy from the total spin S remained. The actual splitting depended on the nature of the field but the lowest level was normally a singlet since any symmetry induced degeneracy was expected to be split by the spontaneous distortion of the Jahn-Teller effect (Jahn and Teller, 1937; van Vleck, 1939; Ham, 1968).

This picture was confirmed by detailed experimentation in the 1950's when, in particular, paramagnetic resonance allowed detailed investigation of the lowest lying states. Originally pioneered by Zavoisky it was brought to maturity by Bleaney and his group in Oxford (Abragam and Bleaney, 1970) using higher frequency microwave sources derived from the wartime radar programme. This work was assisted by parallel theoretical developments. It was Bloch (1946) who had first written down the equations governing the motion of spins driven by an oscillating field which gave the underlying description not only of this phenomenon but that of nuclear magnetic resonance which was to become even more ubiquitous. While its impact in chemistry and beyond has been far greater than that of paramagnetic resonance, it has been more peripheral to the development of magnetism as defined in this talk. It is therefore one of the many topics which must be excluded.

The Bloch equations emphasised the importance of relaxation times in determining the conditions under which resonance could be observed and identified two times, spin-spin relaxation giving the time for the magnetic systems to reach equilibrium, and spin-lattice relaxation giving the time for the magnetic system to come into equilibrium with the heat bath. Gorter and others had also emphasised this problem in connection with adiabatic demagnetisation and van Vleck gave detailed treatments of both phenomenon (see Abragam and Bleaney, 1970).

One of the new features of paramagnetic resonance, first observed by Penrose in 1949 before his untimely death, showed that in dilute crystals hyperfine structure due to the interaction between the magnetic electrons and the nuclear spin could be observed. Observations of these fields at the nucleus were later to be extended using the Mössbauer effect to materials like ferromagnetic metals (Frauenfelder, 1962).

These detailed experiments rapidly demonstrated the shortcomings of the simple crystal field model. It was obvious from a chemical point of view that the d -electrons were involved in covalent bonding with the surrounding ions. It was therefore preferable to regard the transition metal ion and its surrounding ligands which were usually arranged in an octahedral form, as a single complex molecule. The unpaired magnetic electrons occupy antibonding states of the complex with

wave functions concentrated on the magnetic ion but with significant overlap on to the neighbouring ligands (see Fig. 4). This model was essential for the $4d$ and $5d$ systems in order to predict the correct ground state. The spatial extent of the magnetic electrons was further confirmed by the clever experiments of Feher and others (Feher, 1956; see also Abragam and Bleaney, 1970) who showed by ENDOR that they could measure the hyperfine field at the nuclei beyond the initial shell.

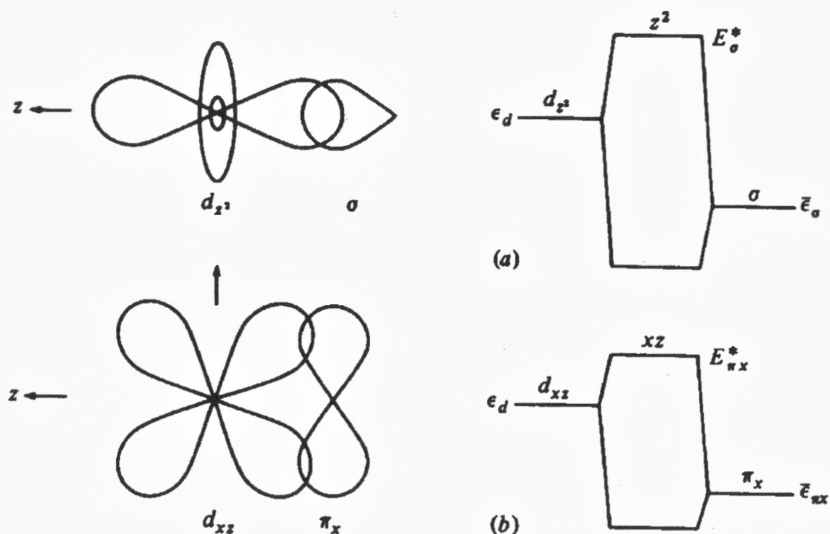


Figure 4. Schematic representation of bonding between d orbitals of two different symmetry types and $s - p$ orbitals on a single ligand. A symmetric combination of these orbitals on the six octahedral neighbours gives bonding and antibonding states with relative energy E^* .

Further complications were revealed by a detailed study of the hyperfine interaction on the magnetic ion. The most striking effect occurred in Mn^{++} ions where the $3d^5$ configuration has an ${}^6S_{\frac{5}{2}}$ ground state which should give zero magnetic field at the nucleus. The large observed result was interpreted by Abragam and Pryce (see Abragam and Bleaney, 1970) as due to admixture of s wave functions which had a density at the nucleus and hence a hyperfine interaction through the contact term.

Thus, although the general behaviour of the energy levels of the paramagnetic ion could be interpreted on the crystal field model, in particular using the symmetry

reflected there, the actual situation was much more complicated and the values of the parameters such as the crystal field splitting itself and the g -factors which gave the Zeeman splitting, together with the hyperfine coupling terms could not easily be calculated from simple models. These parameters were often summarised by a spin Hamiltonian. For example the lowest energy levels of a divalent manganese ion in many salts can be described as follows ($S = 5/2$)

$$\mathcal{H} = \mu\mathbf{H} \cdot \bar{g} \cdot \mathbf{S} + D[3S_z^2 - S(S+1)] + F[S_x^4 + S_y^4 + S_z^4 - (1/5)S(S+1)(3S(S+1) - 1)] \\ + \mathbf{S} \cdot \bar{A} \cdot \mathbf{I},$$

where \bar{g} and \bar{A} are tensors with axial symmetry while the D and F terms reflect the residual results of the crystalline field.

This phenomenological model of the low lying energy states of an isolated paramagnetic ion was further extended by consideration of the exchange interaction between pairs of such ions. Exchange interactions between electrons within an atom were already well understood and detailed calculations were well known in diatomic molecules such as H_2 . In an attempt to find a better analogy for the magnetic systems Slater had made an exhaustive investigation of O_2 which has a $S = 1$ ground state (Magnetism Conference, 1953). But detailed calculations for the magnetic systems were more difficult to make for detailed comparisons with the experimental results which became available from a variety of sources. Heisenberg and Dirac had pointed out that the effect of exchange between two atoms with spin S but no orbital degeneracy could also be written as a spin Hamiltonian

$$\mathcal{H} = -2J(1,2)\mathbf{S}(1) \cdot \mathbf{S}(2),$$

where the sign is conventional so that positive J leads to a preferred parallel alignment. In most cases J turns out to be negative. Also residual orbital effects lead to anisotropy so that J becomes a tensor and $\mathcal{H} = -2\mathbf{S}(1) \cdot \bar{J}(1,2) \cdot \mathbf{S}(2)$. An extreme model which is simpler for theoretical investigation is the Ising model

$$\mathcal{H} = -2I(1,2)S_z(1)S_z(2).$$

Sometimes direct information on J can be obtained from isolated pairs such as occur naturally in copper acetate (Abragam and Bleaney, 1970). In a more normal crystal with a periodic array of magnetic ions the sum of the pairwise interactions leads to a well defined magnetic order.

The magnetic neutron diffraction experiments of Shull and colleagues (1951) showed for the first time the details of the antiferromagnetic order predicted by Néel, from which values of the exchange interactions could be derived. It was clear that the largest interaction came not necessarily between those ions which were

closest as a direct overlap of d wave functions would suggest, but between those ions which had a bridging ligand (see Fig. 5). Thus the overlap of the magnetic electrons onto the neighbouring anions was crucial in explaining the origin of the exchange interaction as discussed originally by Kramers and subsequently developed by Anderson (1950, 1963) and others. It was given the name of superexchange and again it was possible to explain the results phenomenologically by assuming an exchange interaction which was largely isotropic of the Heisenberg type though it also contained some elements of anisotropy. However, fundamental first principle calculations of the value of these exchange parameters proved extremely difficult.

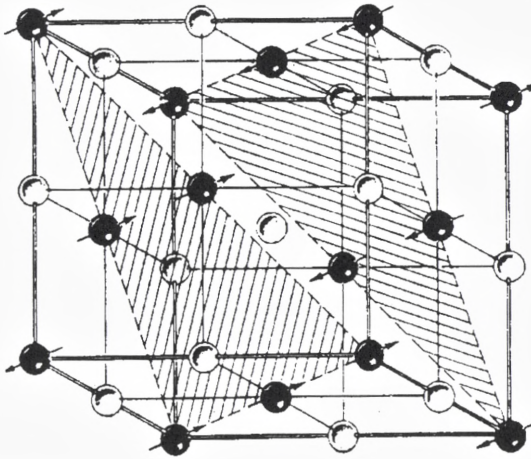


Figure 5. Antiferromagnetic order in MnO. The most strongly coupled spins are antiparallel and have an intervening oxygen ion.

Further information about the detailed value of the exchange parameters became available with experiments which measured the low energy excitations of the ordered magnetic systems. These spin waves which were originally postulated for ferromagnets by Bloch (1930), had been discussed in the antiferromagnetic structures by Kittel and others (Keffer, 1966). Those excitations with wave vector $k = 0$ could be observed by resonance techniques but gave limited information. With the use of the triple axis neutron spectrometer developed by Brockhouse it became possible to observe the spectrum of spin waves across the Brillouin zone and derive the values of the exchange parameters directly from them (see Fig. 6).

One of the other areas which was developed extensively in the 1960's was the

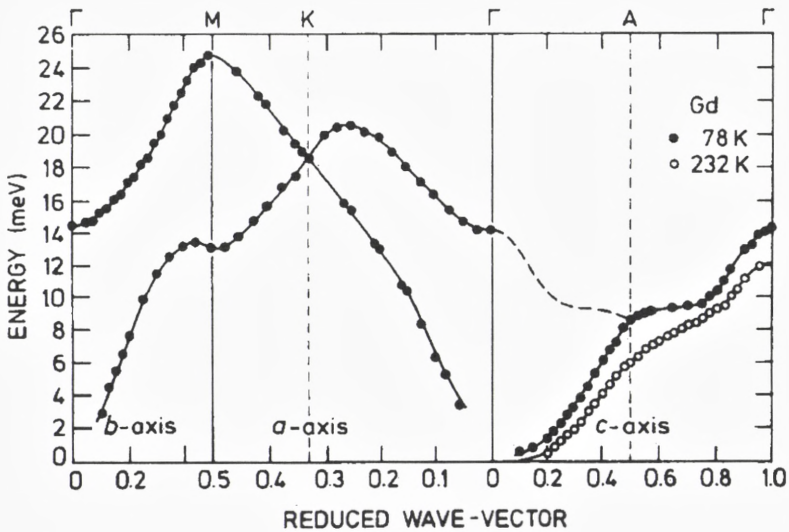


Figure 6. A remarkable example of the complete spin wave spectrum of Gd. (after Koehler et al., 1970).

theoretical and experimental study of the thermodynamic properties of these cooperatively coupled spin systems. The Weiss molecular field theory gave an overall description containing a high temperature paramagnetic phase where the susceptibility was given by the Curie-Weiss law, a transition temperature below which the magnetic order appeared and grew continuously to saturate at $T = 0$. Expansion of the thermodynamic functions in power series of $(1/T)$ gave a more detailed treatment of the high temperature phase (Domb and Green, 1974), while study of the excitations such as spin waves gave a description at low T . In the case of the Ising model, where the low temperature parameter is $\exp(-J/T)$ it was possible to obtain many terms in both expansions, but for the Heisenberg model even the first few terms required a remarkable tour de force (Dyson, 1956). Much effort was expended on extrapolating these expansions towards the singularity which occurred at the transition temperature where fluctuations are important (Fig. 7). The introduction of renormalisation group methods (see Fisher, 1974) allowed a detailed treatment of this singular critical region and magnetic systems proved to be the most appropriate experimental testing ground for these theories. The non-classical behaviour in the region of the critical temperature is more pronounced in low dimensional arrays and so two-dimensional magnetic systems have been extensively studied. In one dimension the fluctuations dominate and no transition

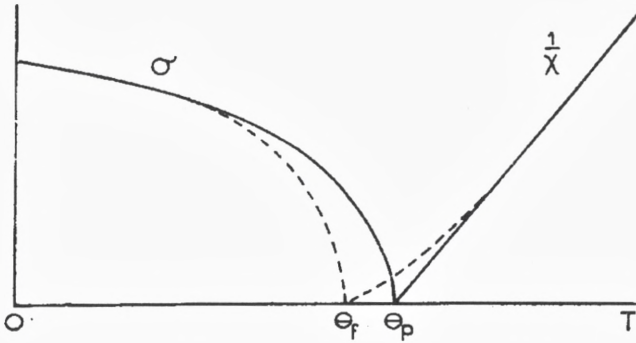


Figure 7. An early representation after Néel in *Le Magnetisme* (1940) of “effect des fluctuations du champ moleculaire...” At $T \rightarrow T_c (= \Theta_f)$ the critical effects give $\chi^{-1} \sim (T - T_c)^\gamma$ with $\gamma > \gamma_0 = 1$ and $\sigma \sim (T_c - T)^\beta$ with $\beta < \beta_0 = 1/2$ where β_0, γ_0 are the mean field values.

occurs although interesting effects occur as $T \rightarrow 0$.

Thus the standard model of individual magnetic ions described basically in terms of their atomic d and f electrons but having some overlap into orbitals on neighbouring ions, and interacting with neighbours through an exchange interaction mediated via that overlap, was developed to give a full and sophisticated description of the magnetic properties of insulators. Its spectacular success tended to divert attention away from the fundamental assumptions which went into the model, which some workers found difficult to accept. This was particularly true for those who came from groups which focussed their attention on understanding the magnetism of the transition metals. Here it was clear, looking no further than the saturation moment of Ni at $0.6 \mu_B$, that an assembly of paramagnetic ions could not provide a satisfactory description. Such work started naturally from band theory where the conduction electrons occupied, to a first approximation, independent states which covered the whole crystal. The answer, of course, lay in the correlation energy brought about by the interaction between the electrons. At the 1952 conference there was an extended and heated discussion summarised by Smoluchowski (*Magnetism Conference, 1953*). [Although not recorded there it included, if my memory serves me correctly, an extensive discussion of the rhetorical question – why is NiO an insulator? It has an odd number of electrons per unit cell and hence cannot have an integral number of filled bands. The doubling of the size of unit itself from antiferromagnetic order is not relevant since the conductivity does not change at the transition temperature. The answer lies in the energy penalty which is required to change a pair of Ni^{2+} ions into Ni^+ and Ni^{3+} .] In the standard model of insulator magnetism it is assumed that this correlation energy is so great that all

such states can be ignored, while at the other end of the scale simple band theory of non interacting electrons assumes that there is no energy penalty at all. Clearly the true situation lies between but because it is so difficult to deal with much of the early period involved discussion between workers who began from one extreme or the other and were unable to meet in the middle.

5 Transition metals

As early as 1934 Stoner (1934) had shown that a plausible model of ferromagnetism in Ni and Fe could be made by introducing the Weiss molecular field into a simple band theory and, moreover, by appropriate choice of parameters it could account non integral saturation moments. This idea was made more realistic by Mott and others by the introduction of both *s* and *d* bands which were hybridised, while the relevant exchange interaction was assumed to act on the *d* components. These ideas could account to a large extent for the properties of alloys as systematised in the Slater–Pauling curves (see Fig. 8). Attempts to calculate the exchange energy were confined to the Hartree–Fock method using simplified concepts introduced by Wigner and others to allow for the fact that the exclusion principle kept electrons of like spin at a greater distance than those of opposite spin. This helped increase the ferromagnetic component of exchange. After the war calculations of band structure gradually improved with the increase in computer power, but even then calculations of the exchange energy were difficult and unreliable even in respect of the sign. The situation was further complicated by the discovery that Cr had a small antiferromagnetic moment while Mn also showed unusual magnetic order patterns (Wilkinson et al., 1962).

Furthermore, the new experimental techniques were providing information which it was easier to interpret in terms of localised moments, similar to those in insulators, than from the simple band theory. Neutron diffraction revealed moment distributions in both elements and alloys which were similar to those observed in salts while spin waves observed initially by ferromagnetic resonance in films and then by inelastic neutron scattering were also found to have properties similar to those in insulators (Lowde, 1956; Seavey and Tannenwald, 1958). Moreover, the behaviour characteristic of localised moments persisted in the fluctuations which were observed around the transition temperature and above. This led to some further controversy between those theoreticians who approached the problem from opposite ends. It was clear that a better treatment of the correlation energy was needed and various models were put forward to try to bridge the gap. van Vleck suggested that this could be achieved by restricting the configurations of the *d*-electrons allowed on each atom but a specific formulation of the problem which

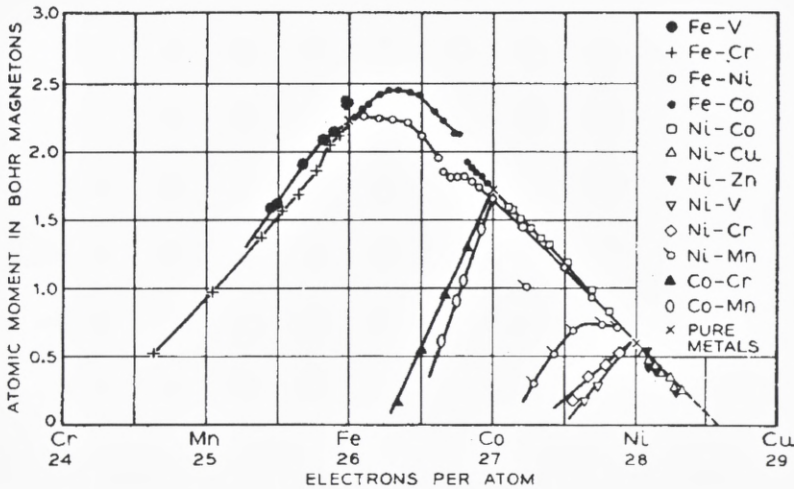


Figure 8. The Slater–Pauling curve of the saturation magnetisation in transition metal alloys plotted as a function of electron concentration which can be broadly interpreted in terms of band filling (after Bozorth, 1951).

allowed detailed evaluation was lacking. Zener (1951) proposed that it was the interaction between the conduction electrons and the d -shells which was mainly responsible for ferromagnetism.

The first major step in resolving this dilemma came from the study of the free electron gas without specific reference to magnetism. The use of diagrammatic techniques in many particle physics began in the early 1950's soon after their introduction into field theory. Using Feynmann diagrams and the Greens function methods of Schwinger the theory of the homogeneous electron gas was worked out by many contributors during the period 1957–8 (Mahan, 1981). Very crudely, the main understanding derived from this was that the long range Coulomb interaction gave rise to collective excitations, the plasmons, at high frequency leaving a gas of effectively free particles with a Fermi distribution and a residual short range screened interaction which resulted in both a further direct and an exchange energy. The low frequency excitations of this system could be regarded as the promotion of quasi particles across the Fermi surface giving rise to what has been described as a Fermi liquid.

The second important step was to concentrate on electrons in bands, as opposed to free electrons, interacting via the short range screened interaction. A great deal was clarified by the Hubbard model (Hubbard, 1963, 1966) which used a single band with electrons in orbitals which were localised around each site (Wannier

functions). If the residual interaction was of sufficiently short range that it was confined to a single atomic site its only component coupled electrons of opposite spin since electrons of the same spin were forbidden by the exclusion principle. The simple Hubbard Hamiltonian takes the form

$$\mathcal{H} = \sum_{\ell} \left[\sum_{\delta} t(\delta) a_{\sigma}^{+}(\ell) a_{\sigma}(\ell + \delta) + U n_{\sigma}(\ell) n_{-\sigma}(\ell) \right],$$

where $a_{\sigma}^{+}(\ell)$ creates an electron on site ℓ with spin σ and $n_{\sigma}(\ell) = a_{\sigma}^{+}(\ell) a_{\sigma}(\ell)$ is the number of such electrons. This has two essential parameters, the band width determined by t and the interaction energy U . A somewhat more realistic model was proposed by Anderson (1961), included both s and d electrons which were hybridised while the interaction energy was assumed to act only between the d -electrons. Here

$$\begin{aligned} \mathcal{H} = & \sum_{\ell\sigma} \epsilon_{d\sigma} n_{d\sigma}(\ell) + U_{\sigma\sigma'} n_{d\sigma}(\ell) n_{d\sigma'}(\ell) + \sum_k \epsilon_s(k) a_s^{+}(k) a_s(k) \\ & + \sum_{k\ell\sigma} A_{sd\sigma}(k) e^{ik \cdot R(\ell)} [a_s^{+}(k) a_{d\sigma}(\ell) + a_{d\sigma}^{+}(\ell) a_s(k)], \end{aligned}$$

where $\epsilon_s(k)$ are the band energies of the s electrons and $A(k)$ gives the hybridisation. By a number of innovative techniques Hubbard obtained approximate solutions to this problem which showed that if t/U was small, i.e. U was large, an insulator was obtained with an effective exchange interaction in the form t^2/U . When U was small the system was effectively still a Fermi gas.

Further evaluation of this model showed that it predicted both individual particle excitations across the Fermi surface and between the Fermi surfaces of different spin, as well as collective excitations in the form of spin waves. It therefore produced, from a single model, properties which were thought to be typical of both the extreme localised and band models. This was important because it was shown (Gold et al., 1971) by de Haas–van Alphen measurements that the ferromagnetic metals did indeed show Fermi surfaces and that these were different for the two spin types. These detailed measurements required further refinement of the band structure calculations but with the rapid evolution of improved numerical techniques reasonable agreement between theory and experiment has been obtained.

A thorough discussion of all aspects of this problem was given by Herring (1966) in his book entitled “Exchange Interactions Among Itinerant Electrons”. In particular he reviews the controversy of the itinerant versus localised spin models of ferromagnetic metals and the experimental properties which require explanation.

6 Rare earth metals

The study of the magnetism of the rare earth metals has proved one of the most interesting and satisfying topics of the post-war years. In the 1930's it had been established that these materials showed, at room temperature, a paramagnetism similar to their salts but that things were much more complicated at low temperatures. In particular gadolinium had been found to be ferromagnetic below room temperature. After the war the topic was boosted by the availability of relatively pure elements obtained by improved separation techniques by Spedding and his colleagues at Ames. But the real breakthrough came in 1960 when Koehler and Wollan showed by neutron diffraction (Koehler et al., 1961) that these materials displayed a wealth of interesting types of magnetic order which had hitherto been unexpected. The heavy metals Gd–Tm showed various magnetic phases where components of the magnetisation varied sinusoidally as one moved from layer to layer along the c axis to give simple helices in Tb, Dy, a cone in Er, and longitudinal wave in Tm (Fig. 9). Moreover, these phases changed as the temperature was lowered in a way which appeared to be controlled by magnetic anisotropy. At high temperatures the wave vector q of the wave varied continuously and was incommensurate with the lattice dimension, at lower temperatures the system locked in to commensurate structures. There was also a distortion reflecting the crystallographic symmetry and a tendency towards ferromagnetic order at the lowest temperature. The magnetic moments were, by and large, those expected for the free ions.

Later experiments elucidated the more complex orderings found in Pr, Nd, and to some extent in Sm. Here the q of the modulation was parallel to the basal plane and had three equivalent axes arising from the hexagonal symmetry. Further complications were induced by the double hexagonal close packed crystal structure which gives two types of ionic site. The elements at the ends and in the middle of the series were anomalous because it was energetically preferred to change the f configuration to a full shell in Lu and a half filled shell in Eu. Ce proved even more interesting since it exists in two phases which broadly correspond to the configuration for f^0 and for f^1 .

The essential outlines of this remarkable behaviour could be broadly understood on the basis of a "standard model" (Jensen and Mackintosh, 1991) in which the magnetism was carried by the f electrons which were strongly correlated so that the configuration was fixed. As in the salts these were subjected to a crystal field reflecting the symmetry of the surroundings. In the heavy rare earths this was predominantly axial with a smaller hexagonal component. The many electron nature of the atomic f^n wave functions meant that for a charge distribution which energetically favoured a quadrupole moment for the electron cloud which lay in the

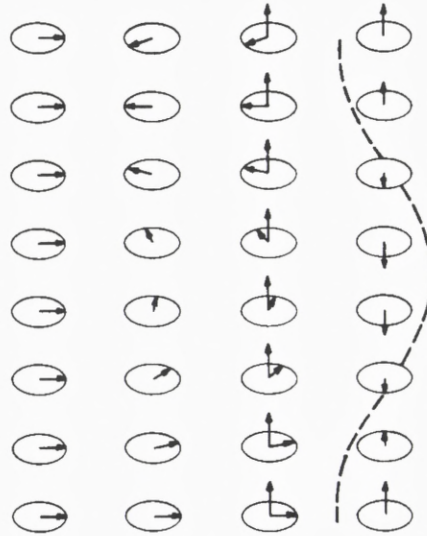


Figure 9. Simple magnetic structures found in the heavy rare earth metals. The moments within each hexagonal layer are parallel and these may be arranged to give a ferromagnet, helix, cone and longitudinal wave respectively. In real systems these are distorted at lower temperature by anisotropy and phase pinning effects.

equatorial plane, the preferred direction of the moments would change from planar to axial between Ho and Er as observed in the magnetic structures. The hexagonal component was responsible for the distortion of the simple helical patterns as the temperature was lowered.

The results suggested that hybridisation between the f electrons and the s - d conduction bands must be small and the main candidate for the origin of the exchange interaction was the polarisation of this conduction electron cloud. Rudermann and Kittel (1954) had shown earlier that the most important coupling between nuclear spins in a metal was of this form and the idea had been extended by Kasuya (1956) and Yosida (1957) to magnetic d and f electrons. In order to favour the observed magnetic ordering it was necessary that the spin susceptibility of the electron gas should peak not at $q = 0$ which would favour ferromagnetism or at the q for a zone boundary which would favour antiferromagnetism but at some intermediate point. This would be facilitated if there was nesting of the Fermi surface where two or more areas were parallel. Over the years calculations of the band structure of these materials have improved to a point where such properties are plausibly predicted Freeman (1972).

Further details of the relevant parameters were evaluated by other methods,

notably the observation of spin waves and the effects of strong applied magnetic fields. These required a number of refinements including anisotropic exchange and magnetostrictive effects but the basic model remained intact as a broad picture. In some ways it is simpler than the transition metals since the f electrons remain strongly correlated and have properties very similar to those in salts while the conduction electrons have well defined Fermi surfaces as has been shown from de Haas–van Alphen measurements (Mattocks and Young, 1977; Wulff et al., 1988) on Gd and Pr.

In all this Allan Mackintosh played a central role. His interest derived from his period in Ames and he made significant contributions to the theory of resistivity and to improved band structure calculations. Later, at Risø, he and his colleagues pushed forward a number of neutron diffraction studies including the observation of magnetic order in Pr which only exists because of the coupling of the nuclear spins to the singlet electronic ground states. All of this is splendidly summarised through his long standing collaboration with Jens Jensen in their book (Jensen and Mackintosh, 1991).

Hybridisation of the f electrons with the conduction electrons is observed in compounds of those elements where the valence is known to vary; notably Ce, Tm, and particularly in uranium in the actinides which exists in compounds with valence varying between three and six. The narrow f bands so generated give rise to a number of interesting effects, the most striking of which is the huge electronic heat capacity associated with large effective masses and hence to the title of heavy fermion compounds, as an alternative to mixed valence compounds. As will be seen from the analysis in Sect. 2 these have enjoyed a significant vogue during the period under review.

Another important phenomena for isolated local moments which have strong interactions with the conduction electrons is the effect named after Kondo (1969) which we can only mention here.

7 Conclusion

The period since the war has seen an enormous growth in the study of magnetism. Ever more sophisticated experiments on a wider and wider group of materials has shown the remarkable richness of the phenomena. The number of people working in the field and the extent of the results available continues to grow. Naturally occurring materials are being overtaken by artificially constructed systems with enhanced desired properties, for example the compounds which give improved hard and soft ferromagnets, the spin glasses, and most recently the multilayers of different magnetic species which show among other effects giant magneto-resistance

(Proc. I.C.M., 1995). But underlying all this are relatively simple concepts which are underpinned by quantum mechanics. For magnetic salts these derive from the unfilled shell configurations d^n, f^n and their interactions with the crystalline electric field of their surroundings and bonding to nearby ligands. The molecular field of Weiss derives from exchange interaction between pairs of such ions. In metallic systems the essential ingredient is the band structure but it must include a treatment of correlation effects in order to give the interesting magnetic properties. The initial success of the theory of insulators based on a phenomenological spin Hamiltonian tended to obscure this point, but more recent work has shown its essential validity. For both models, actual numerical calculations from first principles of the parameters which can be derived from experiment is difficult and has only been achieved in a relatively few cases.

In giving this talk I am conscious of its superficiality and of the large number of areas which it has not been able to address. An obvious one is the magnetism of conduction electrons in semiconductors and metals outside the transition groups. Here much work has been done to elucidate the Fermi surface in metals and to study the Landau ladder of levels expected in semiconductors. The most dramatic consequence of the latter has been the quantum Hall effect but somehow this has not been considered to be "magnetism". One area which does have a magnetic component is the study of high T_c superconductors and these have been extensively reported at Magnetism Conferences. The key element has proved to be CuO planes where the d bands are narrow and the system is almost "mixed valent". At perfect stoichiometry the d holes on the Cu display antiferromagnetism, and only with doping does the superconductivity become apparent.

This paper represents a necessarily personal and idiosyncratic view of the development of magnetism over the last 50 years, coloured as it is by my own perspective and experience. I hope, nevertheless that I have discharged the last request that Allan Mackintosh made to me in a manner which he would have approved – and that it provides an appropriate background for this conference.

References

- Abragam A and Bleaney B, 1970: *Electronic Paramagnetic Resonance of Transition Metals* (Oxford University Press, Oxford)
- Anderson P, 1950: Phys. Rev. **79**, 950
- Anderson P, 1961: Phys. Rev. **124**, 41
- Anderson P, 1963: *Magnetism* (Academic Press, New York) Vol. 1
- Bloch F, 1930: Z. Phys. **61**, 206
- Bloch F, 1946: Phys. Rev. **70**, 460
- Bozorth R, 1951: *Ferromagnetism* (Van Nostrand)
- Colloque Int. de Ferro et Antiferromagnetisme, 1951: J. Phys. Rad. **12**, 149
- Curie P, 1895: Ann. Chim. Phys. (7 series) **5**, 289

- Domb C and Green M, 1974: *Phase Transitions and Critical Phenomena*, (Academic Press, London) Vol. 3
- Dyson F, 1956: Phys. Rev. **102**, 1717
- Feher G, 1956: Phys. Rev. **103**, 824
- Fisher M, 1974: Rev. Mod. Phys. **46**, 597
- Frauenfelder EH, 1962: *The Mössbauer Effect* (Benjamin, New York)
- Freeman A, 1972: in *Magnetic Properties of Rare Earth Metals* (Plenum, New York) p. 245
- Gold A et al., 1971: Int. J. Magn. **2**, 357
- Ham F, 1968: Phys. Rev. **166**, 307
- Herring C, 1966: *Exchange Interactions among Conduction Electrons* (Academic Press, New York) *Magnetism*, Vol. IV
- Hubbard J, 1963: Proc. Roy. Soc. **276**, 238
- Hubbard J, 1966: Proc. Roy. Soc. **296**, 82; *ibid.*, 100
- Jahn H and Teller E, 1937: Proc. Roy. Soc. **A161**, 220
- Kasuya T, 1956: Prog. Theor. Phys. **16**, 45
- Keffer F, 1966: *Handbuch der Physik* (Springer Verlag, New York) Vol. 18
- Keith S and Quédec P, 1992: *Out of the Crystal Maze* (Oxford University Press, Oxford) Chap. 6
- Koehler W, Wollan EO, Wilkinson MK and Cable JW, 1961: *Rare Earth Research* (Macmillan, New York) p. 149
- Koehler W, Child HR, Nicklow RM, Smith HG, Moon RM and Cable JW, 1970: Phys. Rev. Lett. **24**, 16
- Kondo K, 1969: *Solid State Physics* (Academic Press, New York) Vol. 23
- Langevin P, 1905: Ann. Chim. Phys. (8 series) **5**, 70
- Le Magnétisme, 1932: 6th Cons. de Solvay, (Gauthier-Villais, Paris)
- Le Magnétisme, 1940: 3rd Coll. Sci. de C.N.R.S. (Paris)
- Lowde R, 1956: Proc. Roy. Soc. **235**, 305
- Jensen J and Mackintosh AR, 1991: *Rare Earth Magnetism: Structures and Excitations* (Oxford University Press, Oxford)
- Magnetism Conference, 1953: Rev. Mod. Phys. **25**, 1
- Mahan G, 1981: *Many Particle Physics* (Plenum, New York)
- Mattocks P and Young R, 1977: J. Phys. F **7**, 1219
- Proc. I.C.M., 1959: J. Phys. Rad. **20**
- Proc. I.C.M., 1962: J. Phys. Soc. Japan **17** (Suppl. B1)
- Proc. I.C.M., 1964: (Institute of Physics, Bristol)
- Proc. I.C.M., 1968: J. App. Phys. **39**, 363
- Proc. I.C.M., 1971: J. Phys. (Paris) **32** (Suppl. C1)
- Proc. I.C.M., 1974: (Nauka, Moscow) 5 Vols.
- Proc. I.C.M., 1977: Physica **86–88**
- Proc. I.C.M., 1980: J. Magn. Magn. Mater. **15–18**
- Proc. I.C.M., 1983: J. Magn. Magn. Mater. **31–34**
- Proc. I.C.M., 1986: J. Magn. Magn. Mater. **54–57**
- Proc. I.C.M., 1988: J. Phys. (Paris) **49–51**(C8)
- Proc. I.C.M., 1992: J. Magn. Magn. Mater. **104–107**
- Proc. I.C.M., 1995: J. Magn. Magn. Mater. **140–144**
- Rudermann M and Kittel C, 1954: Phys. Rev. **96**, 99
- Seavey M and Tannenwald P, 1958: Phys. Rev. Lett. **1**, 168
- Shull C, Wollan E and Strausen W, 1951: Phys. Rev. **83**, 333
- Stevens K, 1996: *Twentieth Century Physics* (Institute of Physics, Bristol) Chap. 14
- Stoner E, 1934: *Magnetism and Matter*, (Methuen, New York)

- van Leeuwen J, 1921: J. Phys. (Paris) (6 series) **2**, 361
van Vleck JH, 1932: *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, Oxford)
van Vleck JH, 1939: J. Chem. Phys. **7**, 72
Wilkinson M et al., 1962: Phys. Rev. **127**, 2080
Wulff M, Lonzarich GG, Fort D and Skriver H, 1988: Europhys. Lett. **7**, 629
Yosida K, 1957: Phys. Rev. **106**, 893
Zener C, 1951: Phys. Rev. **81**, 440