1.1 A brief history

The quantum theory of magnetism was first placed on a sound footing in 1932 by J.H. Van Vleck in his classic monograph *The Theory of Electric and Magnetic Susceptibilities*. In it, he extended the calculations of the magnetic susceptibilities of isolated rare earth ions, which had been performed by Hund (1925), to encompass the anomalous cases of Eu and Sm, which have low-lying multiplets, giving rise to *Van Vleck paramagnetism*. He was thus able to obtain good agreement with experiment over the whole series from La to 'Casseiopaium' (now Lu). The study of the metallic elements began in earnest when Urbain, Weiss, and Trombe (1935) discovered the *ferromagnetism* of Gd. Klemm and Bommer (1937) determined the *paramagnetic Curie temperatures* of the heavy rare earths and Néel (1938) showed that, in the presence of strong spin–orbit coupling on the ion and an interionic exchange interaction between the spins, these should be proportional, as observed, to $(g-1)^2J(J+1)$. This later became known as the *de Gennes factor*.

Very little work was done on the rare earths during the war, but immediately afterwards F.H. Spedding, at Iowa State University, resumed his programme of producing the pure elements, and by the early 1950s relatively large quantities had become available. One of the first fruits of this programme was the extension of physical measurements to the light rare earths, when Parkinson, Simon, and Spedding (1951) detected a number of anomalies of magnetic origin in the *heat capacity*. Just previously, Lawson and Tang (1949) had showed that the γ–α phase transition in Ce, which can be induced either by pressure or cooling, resulted in no change of the fcc symmetry, but a substantial reduction of the lattice parameter. Zachariasen and Pauling independently ascribed this shrinking to the transfer of the localized $4f$ electron to the conduction band, the so-called *promotional model*. Extensive measurements were carried out on polycrystalline samples of all the stable lanthanides through the 1950s, and summarized by Spedding, Legvold, Daane, and Jennings (1957) at the close of this early period of rare earth research. Of particular significance, in the light of later developments, was the observation of extra magnetic neutron-diffraction peaks in polycrystalline Er by Koehler and Wollan (1955).

The disparate theoretical components which were later brought together to form the *standard model* of rare earth magnetism were also formulated in the 1950s. Zener (1951) suggested that localized moments could be coupled together by an *indirect exchange* through the medium of the conduction electrons, and Ruderman and Kittel (1954) calculated this coupling quantitatively for nuclear moments embedded in a free-electron gas. Kasuya (1956) and Yosida (1957) extended the treatment of this *RKKY interaction* to localized electronic moments. Stevens (1952) invented his method of *operator equivalents*, which was of decisive importance for a satisfactory treatment of the crystal fields. Mason (1954) formulated a theory of *magnetoelastic effects*, while Zener (1954) showed how to calculate the temperature dependence of the magnetic anisotropy.

The classical period of rare earth magnetism was heralded by the publication of the *magnetization* measurements on monocrystalline Dy by Behrendt, Legvold, and Spedding (1957). The fabrication of single crystals of all the heavy rare earths followed successively, and their bulk magnetic properties were studied at Iowa State by Legvold and his students. They were also made available to Koehler and his colleagues at Oak Ridge for *neutron-diffraction* measurements, which revealed what he later described as 'a panoply of exotic spin configurations'. By the time of the First Rare Earth Conference at Lake Arrowhead, California in October 1960, both the magnetic susceptibilities and structures had been extensively investigated. The papers of Legvold (1961) and Koehler, Wollan, Wilkinson, and Cable (1961) summarized the remarkable progress which had been made by that time.

Theoretical developments lagged little behind. Almost simultaneously with the observation of the *helical structure* in Dy, Enz (1960) showed that the magnetization curves implied such a structure, and pointed out the importance of magnetoelastic effects in inducing the transition to the ferromagnetic phase. Niira (1960) successfully interpreted the magnetization of Dy in the ferromagnetic phase by calculating the *spin-wave spectrum* of an anisotropic magnet, showing that a finite energy is required to create a long-wavelength excitation. This *energy gap* gives rise to an exponential decrease of the magnetization at low temperatures. Elliott (1961) considered the magnetic structures of the heavy rare earths and their temperature dependences, utilizing a phenomenological *molecular-field model*. A similar approach was taken by Miwa and Yosida (1961), while Nagamiya, Nagata, and Kitano (1962) calculated the effect of a magnetic field on some of these structures, showing that a *fan* structure may exist between the helix and the ferromagnet. In these papers, the standard model first attained a coherent formulation.

The transport properties, particularly the *electrical resistivity*, were elucidated in the same period. De Gennes (1958) considered the *magnetic disorder scattering*, showing that it is proportional to the de Gennes factor in the paramagnetic phase, while Kasuya (1959) gave a very complete discussion of the same subject, including not only the paramagnetic phase but also scattering by spin waves and rare earth impurities. The first resistivity measurements on single crystals were made on Er by Green, Legvold, and Spedding (1961). The unusual temperature dependence of the resistance in the c-direction was explained by Mackintosh (1962) as a consequence of the incommensurable magnetic ordering, leading to *magnetic superzones*. Miwa (1963) and Elliott and Wedgwood (1963) made calculations of the magnitude of this effect, using the free electron model, which were in semi-quantitative agreement with the experimental results. Mackintosh (1963) pointed out that the spin-wave energy gap should also give rise to an exponential increase in the magnetic scattering at low temperature and deduced that the gap in Tb is about 20 K, a value later substantiated by direct measurements.

Until this time, the conduction electrons in the rare earths had been described by the *free-electron model*, but Dimmock and Freeman (1964) demonstrated that this simplification was unjustified when they calculated the *band structure* of Gd by the APW method. The conduction electrons were found to be largely d-like, as in the transition metals, and the Fermi surface far from spherical. At that time, single crystals of the purity required to allow conventional Fermi surface experiments were unavailable, so Gustafson and Mackintosh (1964) employed *positron annihilation*, initially in polycrystalline samples. Their most striking observation was that the number of $4f$ electrons in Ce does not change greatly at the γ–α transition, in contradiction to the promotional model, and hence to the standard model. Later measurements on single crystals of the heavy rare earths showed that the conduction electrons are indeed far from free electron-like, and the experimental results could be well accounted for by relativistic APW calculations (Williams, Loucks, and Mackintosh 1966).

As the ground-state properties of the rare earth metals became progressively clarified, interest turned towards the *magnetic excitations*. Niira's pioneering theoretical work was followed by the calculation of the spin-wave *dispersion relations* in a variety of heavy-rare-earth magnetic structures by Cooper, Elliott, Nettel, and Suhl (1962). The first observations of spin waves by *inelastic neutron scattering* were made at Risø by Bjerrum Møller and Houmann (1966), who obtained rather complete dispersion relations for Tb at 90 K. During the following years, Bjerrum Møller and his colleagues performed a series of experiments which revealed many novel phenomena, including the temperature- and field-dependence of the *magnon energies*, allowing the deduction of the exchange and its anisotropy, and crystal-field and magnetoelastic parameters. Magnons in the incommensurable helical phase, including *phason* excitations at long wavelengths, were also observed, as was the interaction of magnons with each other, with the conduction electrons, and with phonons, including coupling through a new mechanism involving the spin–orbit interaction of the conduction electrons, explained by Liu (1972a).

Callen and Callen (1963) further developed the theory of *magnetostriction*, putting it in the form used by Rhyne and Legvold (1965a) to interpret their pioneering measurements on single crystals. Callen and Callen (1965) also generalized the treatment of the temperature dependence of crystal-field and magnetoelastic parameters. Cooper (1968a,b) considered in detail the role of the magnetoelastic effects in the helical-ferromagnetic transition, and included them in calculations of the spin-wave energies. Turov and Shavrov (1965) had earlier proposed that, since the magneto-strain cannot follow the precession of the moments in a spin wave, the energy gap should not vanish when the hexagonal anisotropy is cancelled by an external magnetic field. This *frozen lattice* effect was observed by Nielsen, Bjerrum Møller, Lindgård, and Mackintosh (1970). In the late 1960s, the availability of separated isotopes allowed spin-wave measurements at Oak Ridge on a number of the heavy rare earths which, because of neutron absorption in the natural state, could otherwise only be studied with great difficulty. Of particular interest were experiments on the isotropic ferromagnet Gd, in which the *magnetic form factor* was studied by Moon and Koehler (1971) and the spin waves by Koehler, Child, Nicklow, Smith, Moon, and Cable (1970), and the clear evidence for a large *exchange anisotropy* in the *conical phase* of Er (Nicklow, Wakabayashi, Wilkinson, and Reed 1971a).

With the increasing understanding of the magnetic behaviour of the heavy rare earths, it was natural that attention began to turn to the lighter metals. Moon, Cable, and Koehler (1964) began what was destined to become a long-lasting study by a number of groups of the magnetic structure of Nd, and Cable, Moon, Koehler, and Wollan (1964) found indications of antiferromagnetic ordering in polycrystalline Pr. Bleaney (1963) had earlier shown that the crystal-field ground states in Pr should be singlets, and in such *singlet ground-state systems* no magnetic ordering should occur unless the exchange exceeds a critical value. Johansson, Lebech, Nielsen, Bjerrum Møller, and Mackintosh (1970) could indeed detect no signs of magnetic ordering at 4.2 K in monocrystalline Pr. Shortly afterwards, the crystal-field excitations, or *magnetic excitons*, were observed by Rainford and Houmann (1971) and, on the basis of these results, Rainford (1972) proposed a crystal-field level scheme which is very close to that accepted today.

The achievements of the classical period were summarized in the compendium on the *Magnetic Properties of Rare Earth Metals*, edited by R.J. Elliott, which was published in 1972 and, in a sense, also signalled the end of this period. In the modern era, the principles which had been established by the early 1970s have been applied to attaining a deeper and more complete understanding of the elements, even though the primary interest has increasingly turned towards rare earth compounds and alloys. For example, the magnetic interactions in the exchange-dominated system Tb were studied in exhaustive detail with inelastic neutron scattering by Jensen, Houmann, and Bjerrum Møller (1975). The crystal-field dominated system Pr was subjected to a similarly careful investigation by Houmann, Rainford, Jensen, and Mackintosh (1979) and, from his analysis of these results, Jensen (1976a) concluded that Pr could be induced to order antiferromagnetically either by the application of a modest *stress* or, through the *hyperfine interaction*, as first proposed by Murao (1971), by cooling to about 40 mK. The former effect was observed by McEwen, Stirling, and Vettier (1978) while magnetic ordering at very low temperatures had been inferred from heat-capacity measurements by Lindelof, Miller, and Pickett (1975). However, the controversy surrounding this phenomenon was only finally settled by the unambiguous observation of magnetic ordering by neutron diffraction (Bjerrum Møller, Jensen, Wulff, Mackintosh, McMasters, and Gschneidner 1982). The effects of the crystal field alone were studied by Touborg and Høg (1974), by dissolving small amounts of the magnetic rare earths in Sc, Y, and Lu and determining the crystal-field level scheme through susceptibility measurements, in conjunction with inelastic neutron scattering (Rathmann and Touborg 1977).

Efforts to increase the purity of rare earth samples were rewarded by the observation of the *de Haas–van Alphen (dHvA) effect* in Gd by Young, Jordan, and Jones (1973) and the subsequent detailed elucidation of its Fermi surface, which could be satisfactorily accounted for by band structures calculated with the inclusion of the exchange splitting between up- and down-spin levels. More recently, the careful study of the dHvA effect in paramagnetic Pr by Wulff, Lonzarich, Fort, and Skriver (1988) has confirmed the success of the band model in describing the conduction electrons, and given extensive information on their interaction with the $4f$ electrons.

The electronic structure of Ce has been of continued interest. Johansson (1974) elaborated the suggestion of Gustafson, McNutt, and Roellig (1969) that α–Ce is a *4f-band metal*, and Glötzel (1978) and others have further explored this model by band structure calculations. Single crystals of α–Ce suitable for dHvA experiments are extremely difficult to prepare, but Johanson, Crabtree, Edelstein, and McMasters (1981) have studied the related compound $CeSn_3$, observing the $4f$ character of the electrons at the Fermi surface. *Photoemission experiments* by Wieliczka, Weaver, Lynch, and Olson (1982) and Mårtensson, Reihl, and Parks (1982) proved highly informative in exploring the electronic structure of Ce. This work reflects the intense interest in the 1980s in the problem of non-integral $4f$ occupancy, which gives rise to a variety of phenomena subsumed under the description *mixed-valent* behaviour, the most striking of which is the huge electronic heat capacity and associated effective masses measured in *heavy-fermion materials*. The discovery of *superconductivity* in $CeCu_2Si_2$ by Steglich, Aarts, Bredl, Lieke, Meschede, Franz, and Schäfer (1979) stimulated a major effort in studying lanthanide and actinide heavy-fermion systems, and underlined the significance of the earlier observation of superconductivity in Ce under pressure by Probst and Wittig (1975).

The properties of itinerant $4f$ electrons have predominantly been studied through rare earth compounds. Indeed the main thrust of the rare earth research programme has recently been towards understanding *compounds and alloys*, which are generally beyond the scope of this book, but which may nevertheless be largely understood in terms of the principles which we shall present. However, as will be discussed in later sections, there still remain a number of problems in the elements which await and occasionally obtain a solution. For example, the essential features of the classic puzzle of the magnetic structure of Nd have been clarified by McEwen, Forgan, Stanley, Bouillot, and Fort (1985). Gibbs, Moncton, D'Amico, Bohr, and Grier (1985) have re-examined the configurations of the moments in Ho and other heavy rare earths, using a combination of *synchrotron radiation*, which shows promise for very high-resolution structural studies, and neutron diffraction. They utilized the concept of *spin slips* to explain their results, and hence refocused attention on *commensurable magnetic structures*, which had originally been studied by Koehler, Cable, Wilkinson, and Wollan (1966). Initial studies of the excitations of such structures were performed by Larsen, Jensen, and Mackintosh (1987), who thereby explained the long-standing mystery of the stability of the cone structure in Ho at low temperatures. Other unexplained features of the neutron diffraction patterns from Ho were accounted for by Jensen and Mackintosh (1990), who showed that intermediate structures, which they named *helifans*, could be stabilized by a magnetic field.

A new field of endeavour has been opened by the fabrication of *multilayers* of different species of rare earths and the study of their properties by Majkrzak, Cable, Kwo, Hong, McWhan, Yafet, Waszczak, and Vettier (1986), and by Salamon, Sinha, Rhyne, Cunningham, Erwin, Borchers, and Flynn (1986). The size of the teams working on a number of these modern projects in rare earth research reflects the technical complexity of the problems now being tackled, and no doubt also the collaborative spirit of the age.