

# Quantum mechanics—The key to understanding magnetism

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The existence of magnetic materials has been known almost since prehistoric times, but only in the 20th century has it been understood how and why the magnetic susceptibility is influenced by chemical composition or crystallographic structure. In the 19th century the pioneer work of Oersted, Ampère, Faraday, and Joseph Henry revealed the intimate connection between electricity and magnetism. Maxwell's classical field equations paved the way for the wireless telegraph and the radio. At the turn of the present century Zeeman and Lorentz received the second Nobel Prize in physics for, respectively, observing and explaining in terms of classical theory the so-called normal Zeeman effect. The other outstanding early attempt to understand magnetism at the atomic level was provided by the semi-empirical theories of Langevin and Weiss. To account for paramagnetism, Langevin in 1905 assumed in a purely *ad hoc* fashion that an atomic or molecular magnet carried a permanent moment  $\mu$ , whose spacial distribution was determined by the Boltzmann factor (Langevin, 1905a and b). It seems today almost incredible that this elegantly simple idea had not occurred earlier to some other physicist inasmuch as Boltzmann had developed his celebrated statistics over a quarter of a century earlier. With the Langevin model, the average magnetization resulting from  $N$  elementary magnetic dipoles of strength  $\mu$  in a field  $H$  is given by the expression

$$M = \frac{N\mu \iint \cos\theta e^{\mu H \cos\theta / kT} d\omega}{\iint e^{\mu H \cos\theta / kT} d\omega} = NL \left( \frac{\mu H}{kT} \right),$$

where

$$L(x) = \coth x - \frac{1}{x}. \quad (1)$$

At ordinary temperatures and field strengths, the argument  $x$  of the Langevin function can be treated as small compared with unity. Then  $L(x) = \frac{1}{3}x$ , and Eq. (1) becomes

$$M = N(\mu^2 / 3kT)H \quad (2)$$

so that the magnetic susceptibility  $\chi = M/H$  is inversely proportional to temperature, a relation observed experimentally for oxygen ten years earlier by Pierre Curie (1895) and hence termed Curie's law.

To explain diamagnetism, Langevin took into account the Larmor precession of the electrons about the magnetic field, and the resulting formula for the diamagnetic susceptibility is

$$\chi = -\frac{Ne^2}{6mc^2} \sum_i \langle r_i \rangle^2, \quad (3)$$

where  $\langle r_i \rangle^2$  is the mean square radius of an electron orbit, and the summation extends over all the electrons in the atom. The important thing about Eq. (3) is that, in substantial agreement with experiment, it gives a diamagnetic susceptibility independent of temperature, provided the size of the orbits does not change.

Two years later, in 1907, Pierre Weiss, another French physicist, took the effective field acting on the atom or molecule to be the applied field augmented by a mysterious internal or molecular field proportional to the intensity of magnetization (Weiss, 1907). The argument of the Langevin function then becomes  $\mu(H + qM)/kT$  rather than  $\mu H/kT$ , and in place of Eq. (2) one has

$$\chi = \frac{M}{H} = \frac{N\mu^2}{3k(T - T_c)}, \quad (4)$$

where

$$T_c = \frac{Nq\mu^2}{3k}.$$

Since the right side of Eq. (4) becomes infinite for  $T = T_c$ , the Weiss model predicts the existence of a Curie point below which ferromagnetism sets in. This model also describes qualitatively quite well many ferromagnetic phenomena. Despite its many successes there was one insuperable difficulty from the standpoint of classical electrodynamics. Namely, the coefficient  $q$  of the molecular field  $qM$  should be of the order  $4\pi/3$  whereas it had to be of the order  $10^3$  to describe the observed values of  $T_c$ .

There was, however, an even worse difficulty. If one applies classical dynamics and statistical mechanics consistently, a very simple calculation, which can be made in only a few lines (but I shall not reproduce it here), shows that the diamagnetic and paramagnetic contributions to the susceptibility exactly cancel. Thus there should be no magnetism at all. This appears to have been first pointed out by Niels Bohr in his doctoral dissertation in 1911,<sup>1</sup> perhaps the most deflationary publication of all time in physics. This may be one reason why Bohr broke with tradition and came forth with his remarkable theory of the hydrogen spectrum in 1913. That year can be regarded as the debut of what is called the old quantum theory of atomic structure, which utilized classical mechanics supplemented by quantum conditions. In particular it quantized angular momentum

<sup>1</sup>Reprinted in Vol. I of his collected works. The vanishing of the susceptibility in classical statistics was also proved independently with a slightly different method by J. H. van Leeuwen (1919, 1921).

and hence the magnetic moment of the atom, as was verified strikingly in the molecular beam experiments which were performed by Gerlach and Stern (1922). Hence there was no longer the statistical continuous distribution of values of the dipole moment which was essential to the proof of zero magnetism in classical theory. When Langevin assumed that the magnetic moment of the atom or molecule had a fixed value  $\mu$ , he was quantizing the system without realizing it, just as in Molière's *Bourgeois Gentleman*, Monsieur Jourdain had been writing prose all his life, without appreciating it, and was overjoyed to discover he had been doing anything so elevated. Magnetism could be understood qualitatively in terms of incomplete shells of electron orbits, and a sentence of Bohr which I like to quote reads "In short an examination of the magnetic properties and colors of the long periods gives us a striking illustration of how a wound in the otherwise symmetrical inner structure of the atom is first created and then healed." However, with the passage of time it became increasingly clear that the old quantum theory could give quantitatively correct results for energy levels or spectral frequencies only in hydrogen. One historian of science has referred to the early 1920s as the crisis in quantum theory, but I would characterize this era as one of increasing disillusion and disappointment in contrast to the hopes which were so high in the years immediately following 1913.

The advent of quantum mechanics in 1926 furnished at last the real key to the quantitative understanding of magnetism. I need not elaborate on the miraculous coincidence of three developments, the discovery of the matrix form of quantum mechanics by Heisenberg and Born, the alternative but equivalent wave-mechanical form by de Broglie and Schrödinger, and the introduction of electron spin by Uhlenbeck and Goudsmit. A quantum mechanics without spin and the Pauli exclusion principle would not have been enough—one wouldn't have been able to understand even the structure of the periodic table or most magnetic phenomena. Originally spin was a sort of appendage to the mathematical framework, but in 1928 Dirac synthesized everything in his remarkable four first-order simultaneous equations. To stress the importance of the quantum-mechanical revolution, I cannot do better than to quote an often-mentioned sentence from one of Dirac's early papers, which reads "*The general theory of quantum mechanics is now almost complete. The underlying physical laws necessary for the mathematical theory of a large part of physics and all of chemistry are thus completely known.*"

With at last the key available for the proper analysis of what was going on inside the atom, it was natural that more than one physicist would try applying it to a particular problem. So it is not surprising that four different researchers independently calculated and reported in practically simultaneous publications (Kronig, 1926; Mannebach, 1926; Mensing and Pauli, 1926; Van Vleck, 1926) the susceptibility of a rotating diatomic molecule carrying a permanent dipole moment, which could be either electric or magnetic depending on whether one was interested in an electric or magnetic susceptibility. The new mechanics happily restored the factor  $\frac{1}{3}$  in the Langevin formula (or the correspond-

TABLE I. Value of  $C$  in relation  $\chi = CN\mu^2/kT$ .

Value of $C$	Form and year of theory
$\frac{1}{3}$	Classical, 1905
1.54	Whole quanta, 1921
4.57	Half quanta, 1924
$\frac{1}{3}$	Quantum mechanics, 1926

ing Debye expression in the electric case), as shown in Table I. Thus was ended the confusion of the old quantum theory, where half quanta worked better in band spectra even though whole integers were required with rational application of Bohr's 1913 ideas.

There are three common paramagnetic gases, viz.,  $O_2$ ,  $NO_2$ , and  $NO$ . I shall discuss  $NO$  first as its behavior is the most interesting of the three. In 1926 Robert Mulliken, who has a sixth sense for deducing molecular energy levels from band spectra, had decided that the ground state of the  $NO$  molecule was a  $^2\Pi$  state, whose two components were separated by about  $122\text{ cm}^{-1}$ , but he wasn't sure whether the doublet was regular rather than inverted. I tried calculating the susceptibility of  $NO$  on the basis of Mulliken's energy levels and found (Van Vleck, 1927a and b, 1928) that the observed susceptibility at room temperatures could be explained on the basis that the doublet was regular, i.e., the  $^2\Pi_{1/2}$  component lower than the  $^2\Pi_{3/2}$ . I wasn't entirely convinced that the agreement was real rather than spurious, as molecular quantum mechanics was then in its infancy. If the theory was correct there should be deviations from Curie's law, and so measurements on the susceptibility as a function of temperature should be decisive. To my surprise, experiments to test this prediction were performed in 1929 at three different laboratories in different parts of the world, with each going to a lower temperature than the preceding (Bitter, 1929; Aharani and Scherrer, 1929; Wiersma *et al.*, 1929). As shown in Fig. 1 the accord with theory was gratifying. The ordinate in Fig. 1 is not the susceptibility itself, but rather the effective magneton number  $\mu_{\text{eff}}$  defined by  $\chi = N\mu_{\text{eff}}^2/3kT$ , where  $\beta$  is the Bohr magneton  $he/4\pi mc$ . The nonconstancy of  $\mu_{\text{eff}}$  is a measure of the deviation from Curie's law.

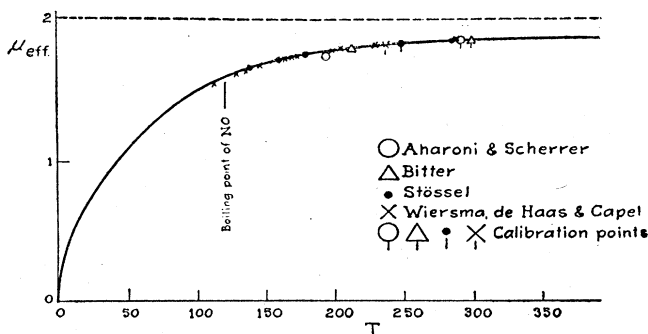


FIG. 1. The effective magneton number (measured in multiples of the Bohr unit  $\beta = he/4\pi mc$ ) of nitric oxide as a function of temperature. Were Curie's law valid, the curve would be a horizontal straight line.

My calculations on NO started me thinking on the general conditions under which Curie's law should be valid or nonvalid. I noted the fact, often overlooked in those early days, that to make a proper computation of the susceptibility even in weak fields, it is necessary to know the energy of the stationary states, or alternatively the partition function, to the second order in the field strength  $H$ , corresponding to including the second as well as first-order Zeeman effect. If the energy of a stationary state is

$$E_i = E_i^{(0)} + E_i^{(1)}H + E_i^{(2)}H^2 + \dots,$$

the correct formula for the susceptibility is

$$\chi = \frac{N}{\sum_i \rho_i} \sum_i \left( \frac{E_i^{(1)2}}{kT} - 2E_i^{(2)} \right) \rho_i, \tag{5}$$

with  $\rho_i = \exp\left(\frac{-E_i^{(0)}}{kT}\right)$ .

Perturbation theory tells us that

$$E_i^{(1)} = \langle i | \mu_H | i \rangle, E_i^{(2)} = \sum_j \frac{|\langle i | \mu_H | j \rangle|^2}{h\nu_{ij}} \quad (j \neq i), \tag{6}$$

where  $h\nu_{ij}$  is the energy interval  $E_i^{(0)} - E_j^{(0)}$  spanned by the matrix element  $\langle i | \mu_H | j \rangle$  of the magnetic moment in the direction of the field  $H$ . From Eqs. (5) and (6) one derives (Van Vleck, 1927a and b, 1928) the results presented in Table II.

In connection with the above it is to be understood that the relevant  $h\nu_{ij}$  are only those which relate to the energy intervals spanned by  $\langle i | \mu_H | j \rangle$ , which because of selection principles can often be less than the total spread in the populated energy levels.

From too cursory an examination of Eq. (5) one might conclude that case (a) could never arise when there is a second-order Zeeman effect, but this is not so. Since  $h\nu_{ij} = -h\nu_{ij} |\langle i | \mu_H | j \rangle|^2 = |\langle j | \mu_H | i \rangle|^2$  the various terms in Eq. (4) can be so paired as to involve a factor  $(\rho_j - \rho_i)/h\nu_{ij}$  which is approximately  $\frac{1}{2}(\rho_i + \rho_j)/kT$  if  $|h\nu_{ij}| \ll kT$ . The fact that the factor  $h\nu_{ij}$  has thereby disappeared shows that there is no catastrophe in the expression for the susceptibility even when the denominators in Eq. (6) for the second-order perturbed energy are very small.

The NO molecule, as we have seen, is an illustration of situation (d). On the other hand, the O<sub>2</sub> and NO<sub>2</sub> molecules are examples of (a) and hence obey Curie's law. The oxygen molecule exhibits the same susceptibility as though its spin of unity ( $S=1$ ) were completely uncoupled from the molecule. Actually the spin is coupled to the molecule so that most of the Zeeman energy becomes of the second rather than first order, but this complica-

tion is immaterial as regards the susceptibility since the binding energy is only of the order  $2 \text{ cm}^{-1}$ , small compared to  $kT$ . The third common paramagnetic gas NO<sub>2</sub> should have a susceptibility corresponding to a free spin  $\frac{1}{2}$ , as it is an odd molecule. Existing data were in disagreement with this prediction when I made it, but new magnetic measurements made by Havens at Wisconsin at my suggestion removed this discrepancy (Havens, 1932).

In 1925 Hund wrote a paper on the magnetic susceptibilities of rare-earth compounds which was the crowning achievement of the empiricism of the old quantum theory (Hund, 1925). He utilized Landé's then phenomenological  $g$  factor and the Hund rule that the state of lowest energy was that of maximum spin, and of maximum  $L$  compatible with this  $S$ . At the time this rule was an inspired conjecture, but today physicists justify it by examining nodes in the wave function. He thus obtained the formula

$$\chi = N \beta^2 J(J+1)g^2/3kT$$

for the susceptibility, and found that this expression agreed remarkably well with experiments for all the trivalent rare-earth compounds except those containing Sm or Eu. In 1928 Laporte pointed out that for these particular two ions, the multiplet structure is such that the interval separating the lowest multiplet component from the one next above it is not large compared to  $kT$  (Laporte, 1928). So he summed Hund's expression for  $\chi$  over the multiplet's various values of  $J$  weighted in accordance with the Boltzmann factor. Even so, he was not able to raise the susceptibility to the values found experimentally. When I read his paper it occurred to me that probably the cause for the discrepancy was that the second-order energy had been omitted. So Frank and I made the relevant calculations (Van Vleck and Frank, 1929; Frank, 1932, 1935), and then there was agreement with experiment, as shown in Fig. 2. The reason that Hund was able to obtain agreement with experiment for other rare earths was that his empirical expression for the first-order energy was the same as

TABLE II. Behavior of the susceptibility in various situations.

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|-----|--|
| (a) | $\chi$ is proportional to $1/T$ if all $ h\nu_{ij} $ are $\ll kT$ .              |
| (b) | $\chi$ is independent of $T$ if all $ h\nu_{ij} $ are $\gg kT$ .                 |
| (c) | $\chi = A + B/T$ if all $ h\nu_{ij} $ are either $\gg kT$ or $\ll kT$ .          |
| (d) | no simple dependence of $\chi$ on $T$ if $ h\nu_{ij} $ is comparable with $kT$ . |

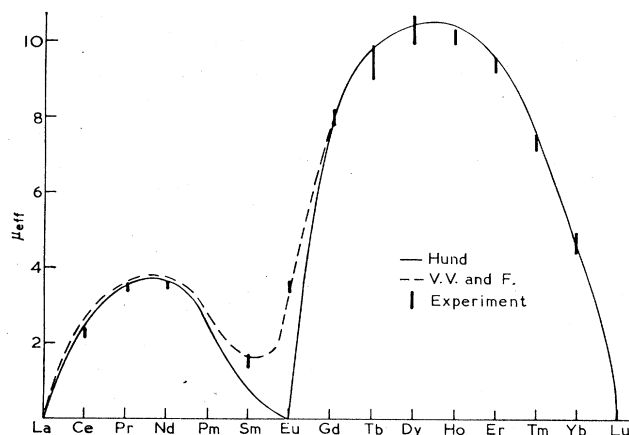


FIG. 2. The effective magneton number (in multiples of  $\beta$ ) at room temperature for the sequence of trivalent ions in the configurations  $4f^0, 4f, 4f^2, \dots, 4f^{14}$ .

the true quantum-mechanical one, and that the second-order could be omitted without too much error. The latter was the case because the interval separating the lowest multiplet component from the next one above is large except for  $\text{Sm}^{3+}$ ,  $\text{Eu}^{3+}$ , and the second-order energy involves this interval in the denominator. Since  $\text{Sm}^{3+}$  and  $\text{Eu}^{3+}$ , unlike the other rare-earth ions, correspond to case (d) or Table II, deviations from Curie's law are to be expected for salts containing these ions. This was indeed confirmed by the limited amount of experimental data available at the time.

In 1930 and 1931 a great deal of my time went into writing my book on the *Theory of Electric and Magnetic Susceptibilities*, which appeared in 1932 (Van Vleck, 1932a). In this volume I aimed to include the major theoretical developments which had taken place up to the time of writing. Besides the things which I have already mentioned, there were other major developments in the theory of magnetism in the early days of quantum mechanics. Heisenberg (1928) took the mystery out of the then twenty year old Weiss molecular field. He showed that it arose from exchange effects connecting the different magnetic atoms, which had the effect of introducing the needed strong coupling between the spins. Other notable theoretical developments prior to 1932 included Landau's paper (Landau, 1930; see also Teller, 1931) on the diamagnetism of free electrons, in which he showed that spinless free electrons had a small susceptibility of diamagnetic sign, in contrast to the zero result of classical mechanics. Pauli (1927) showed that the spin moment of conduction electrons gives rise to only a small paramagnetic susceptibility practically independent of temperature. This paper was notable because it was the first application of Fermi-Dirac statistics to the solid state. If one used the Boltzmann statistics one would have a large susceptibility obeying Curie's law.

On the other hand, there were some important developments which arrived just a little too late for me to include in my volume. Néel's first paper on antiferromagnetism appeared in 1932, and in later years he introduced an important variant called ferrimagnetism, in which the antiparallel dipoles are of unequal strength, so that they do not compensate and the resulting behavior can be ferromagnetic (Néel, 1932; 1936). There was also Peierls' (1933) theoretical explanation of the de Haas-van-Alphen effect, and Bloch's paper (1932) on the width of the boundaries (now called Bloch walls) separating the elementary domains in ferromagnetic materials. The corresponding domain structure was explained and elaborated by Landau and Lifshitz (1935) two years later.

In 1930 I held a Guggenheim fellowship for study and travel in Europe. I spent most of the time in Germany, but by far the most rewarding part of the trip scientifically was a walk which I took with Kramers along one of the canals near Utrecht. He told me about his own theorem (Kramers, 1930) on degeneracy in molecules with an odd number of electrons and also of Bethe's long paper (1929) concerned with the application of group theory to the determination of the quantum-mechanical energy levels of atoms or ions exposed to a crystalline electric field, and in my book I referred to

the role of the crystalline field only in a qualitative way, stressing the fact that it could largely suppress the orbital part of the magnetic moment in salts of the iron group. In the process of writing I did not have the time or energy to attempt quantitative numerical computations. I was most fortunate when, beginning in the fall of 1931, I had two postdoctoral students from England, namely, William (now Lord) Penney and Robert Schlapp. I suggested to these two men that they make calculations, respectively, on salts of the rare earth and of the iron group. The basic idea of the crystalline field potential is an extremely simple one, namely, that the magnetic ion is exposed not just to the applied magnetic field but experiences in addition a static field which is regarded as an approximate representation of the forces exerted upon it by other atoms in the crystal. The form of the crystalline potential depends on the type of crystalline symmetry. For some of the most common types of symmetry the terms of lowest order in  $x, y, z$  are, respectively,

$$\text{axial, tetrahedral, or hexagonal } A(x^2 + y^2 - 2z^2) \quad (7a)$$

$$\text{rhombic } Ax^2 + By^2 - (A+B)z^2 \quad (7b)$$

$$\text{cubic } D(x^4 + y^4 + z^4 - \frac{3}{5}r^4) \quad (7c)$$

If the potential satisfies Laplace's equation, the factors  $A, B, D$  are constants, but because of charge overlap they can be functions of the radius.

The  $4f$  electrons responsible for the magnetism of the rare earths are sequestered in the interior of the atom, and so experience only a small crystalline field. The general formalism which I developed in 1927 and which is displayed in Table II shows that it is a good approximation to treat the atom as free provided the decomposition of the energy levels caused by the crystalline field is small compared to  $kT$ . This condition is fulfilled fairly well for the rare earths at room temperatures, and explains the success of Hund's theory. At low temperatures inclusion of the crystalline potential is usually imperative, and so Penney utilized it to interpret the existing experimental data mainly by Cabrera and by Becquerel. Figure 3 is taken from the original paper of Penney and Schlapp (1932). The ordinate is the reciprocal of the susceptibility. Hence for  $\text{Nd}^{3+}$  one expects it to approach zero as  $T \rightarrow 0$  inasmuch as  $\text{Nd}^{3+}$  is an ion with an odd number of electrons, and even at

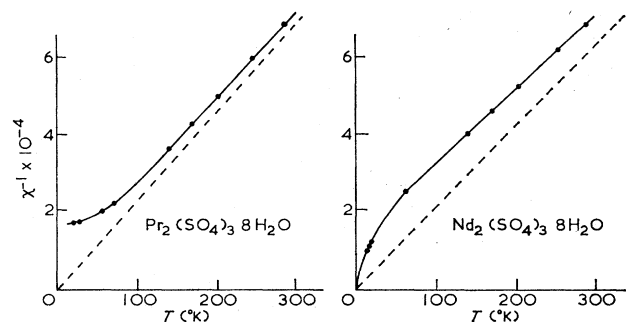


FIG. 3. The reciprocal of the susceptibility as a function of temperature for two rare-earth compounds containing, respectively, an even and odd number of electrons.

$T=0$  there is still the Kramers degeneracy which implies a first-order Zeeman effect and a  $1/T$  term in the susceptibility. On the other hand for the even ion  $\text{Pr}^{3+}$  a sufficiently asymmetrical field should completely lift the degeneracy [case (b) of Table II] and the susceptibility should remain finite as one approaches  $T=0$ . This difference is strikingly exhibited in the two sides of Fig. 3.

When applied to the iron group the results of crystal field theory are particularly striking and form the basis of much of what may be called modern magnetochemistry. The crystalline potential is much larger than for the rare earths and is so powerful that it quenches a large part of the orbital part of the magnetic moment even at room temperatures. Schlapp found that the magnetic behavior in the iron group required a large crystalline field of nearly (but usually not entirely) cubic symmetry.

Each time I read the paper of Schlapp and Penney (1932) I am impressed with how it contains all the essential ingredients of modern crystalline field theory, although there have been changes in the best quantitative estimate of  $D$  in (7c). For instance, it accounted for the fact that most nickel salts are nearly isotropic magnetically and follow Curie's law down to quite low temperatures, whereas the corresponding cobalt salts are highly anisotropic and deviate greatly from Curie's law. However, for a while we thought that there was a difficulty and inconsistency. Let us focus our attention on the ions which are in  $F$  states. In a nearly cubic field an  $F$  state will decompose in the fashion shown in Fig. 4. If a nondegenerate level is deepest, as in Fig. 4, then the orbital moment is completely quenched, and there should be almost complete isotropy. On the other hand, if Fig. 4 is upside down, and if the components  $a, b, c$  of the ground level do not coincide because of deviations from cubic symmetry, and so have different Boltzmann factors, the anisotropy will be considerable. The very different behavior of nickel and cobalt can thus be explained if it is supposed that Fig. 4 is rightside up for  $\text{Ni}^{2+}$  but is upside down in  $\text{Co}^{2+}$ . The calculations of Schlapp then worked fine. However, this seemed to us for a while a thoroughly dishonest procedure, as it appeared to require a change in the sign of  $D$ .

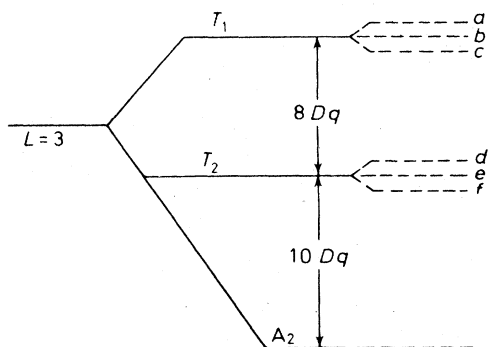


FIG. 4. Orbital energies of an  $F$  state in a nearly cubic field. The decompositions ( $a-b-c$ ) and ( $d-e-f$ ) ensue only because of deviations from cubic symmetry. The quantity  $Dq$  is connected with the constant  $D$  of Eq. (7c) by the relation  $Dq=2D\langle r^4 \rangle/105$ .

Then one day it dawned on me that a simple calculation based on the invariance of the trace shows that the splitting pattern does indeed invert in going from nickel to cobalt even though the constant  $D$  is nearly the same.

The article (Van Vleck, 1932b) in which I published this result is my favorite of the various papers I've written as it involved only a rather simple calculation, and yet it gave consistency and rationality to the apparently irregular variations in magnetic behavior from ion to ion.

The iron group salts I have discussed are of the six-coordinated type, e.g.,  $\text{Co}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ . A simple electrostatic calculation made by Gorter (1932) shows that the constant  $D$  in (7c) should change sign when the coordination is fourfold rather than sixfold and then Fig. 4 should be upright in  $\text{Co}^{2+}$  and inverted in  $\text{Ni}^{2+}$ . Krishnan and Mookherji (1937) verified experimentally this theoretical prediction. They prepared some tetra-coordinated cobalt compounds, which are a beautiful cobalt blue in color, and found that they indeed show very much less anisotropy than do the pink six-coordinated ones.

In 1935 I published a paper in which I amplified and generalized in two respects the primitive crystal field theory employed a few years previously by Penney, Schlapp, and myself. In the first place I showed that Bethe's grouping of energy levels according to symmetry type was still valid even if one allowed the electrons in the unclosed shells to wander away sometimes from the central paramagnetic ion and take a look at the diamagnetic atoms clustered around it. In more technical language, the wave function of the electron has mixed into it small terms which correspond to such excursions. This generalization corresponds to the use of molecular rather than atomic orbitals. Following Ballhausen (1962)<sup>2</sup> it is convenient to designate this more general model as ligand rather than crystal field theory, as chemists sometimes refer to the neighboring atoms clustering about the central ion as ligands. The use of ligand in distinction from crystal field theory can also be characterized as making allowance for incipient covalence.

The other modification I made of the conventional theory was to note that, under certain conditions, the levels may be split so much by the crystalline field as to break down the Hund rule that the deepest state is that of maximum multiplicity permitted by the Pauli principle. This situation is shown schematically in Fig. 5, which is drawn for the configuration  $d^5$ . According to the Hund rule the deepest state is  ${}^6S$  ( $S=2$ ) and this necessitates all but one of the five Stark components being singly inhabited, as in the left side of Fig. 5. However, obviously the energy in the crystalline or ligand field is lower if the three deepest Stark components are doubly populated, with antiparallel spin because of the exclusion principle. However, then the resultant spin is only 0, the Russell-Saunders coupling is broken up,

<sup>2</sup>C. J. Ballhausen, *Introduction to Ligand Field Theory* (McGraw-Hill, New York). This volume is recommended as an excellent survey of the subject, including comparison with experiment.

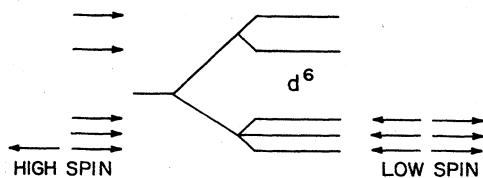


FIG. 5. The central diagram of the figure shows the decomposition of a single  $3d$  level in a field of mainly cubic symmetry. The arrows indicate how the different crystalline field components are filled in case the ion contains six  $3d$  electrons, and also the direction of alignment of each spin. The situation in the left side of the figure represents conformity to the Hund rule, while the right exemplifies what happens when minimization of the energy in the crystalline field is so important as to break down this rule.

and the part of the energy not associated with the crystalline field is raised. The two cases represented by the two sides of Fig. 5 are sometimes referred to as the high and low spin cases. When the susceptibility of a compound is found to conform to the low rather than high spin situation, this is something of interest to chemists. It shows that the interatomic bonding is strong, since it is large enough to break down the Hund rule. Beginning with Pauling and Coryell (1936), this magnetic criterion has even been used to study the chemical behavior of iron in blood. For example, the ferrohaemoglobin ion exhibits high and low spin values 2 and 0 in the presence of  $H_2O$  and  $O_2$  molecules, respectively. I should by all means mention that prior to my own paper Pauling (1931) also stressed the role of covalency effects in magnetism, and the fact that sometimes the low rather than high spin case may be realized. However, in my opinion the method of electron pair bonds which he employed is less flexible and realistic without some modification than is that of molecular orbitals which I used.

In 1937 Jahn and Teller established a remarkable theorem that when in a crystal there is a degeneracy or coincidence of levels for reasons of symmetry, the ligands experience forces which distort the crystalline arrangement, thereby lowering both the symmetry and the energy (Jahn and Teller, 1937).

I realized that the Jahn–Teller effect might have an important effect on magnetic susceptibilities, and in 1939 I published a paper on this subject (Van Vleck, 1939). The energetic effect of Jahn–Teller distortions is very similar to that of molecular vibrations. Consequently I was able to make the calculations which I performed do double duty, using them also in connection with the theory of paramagnetic relaxation caused by spin–lattice coupling. The work I have discussed so far has all related primarily to static susceptibilities but when I visited Leiden in 1938, Gorter aroused my interest in the behavior of the susceptibility at radio frequencies and related problems in relaxation. In a landmark pioneer paper written in 1932 Waller showed that there could be a transfer of energy between the magnetic and phonon systems because of the modulation of the dipolar energy by the lattice vibrations (Waller, 1932), and a little later Heitler and Teller (1936), Fierz (1938), and Kronig (1939) showed that there could be a

similar relaxation effect, usually of larger magnitude, because of the vibrational modulations of the energy associated with the crystalline potential. I made a more detailed explicit calculation (Van Vleck, 1940a) of the numerical values of the relaxation times to be expected for titanium, chromium, and ferric ions. On the whole the agreement with experiment was rather miserable. In an attempt to explain away part of the disagreement, I suggested in another paper (Van Vleck, 1940b) that there might be what is usually called a phonon bottleneck. The point is that because of the conservation of energy only a portion of all the phonons, those in a narrow frequency range, can exchange energy with the spin or magnetic system. Because of their limited heat capacity, these phonons are easily saturated and brought to the same temperature as the spin system, except insofar as they exchange energy by anharmonic processes coupling them to other oscillators, or transport the excess energy to a surrounding bath that serves as a thermostat. Consequently the relaxation process may be considerably slower than one would calculate otherwise.

This brings me up to the years of World War II, during which very little was done in the way of pure research. Even before the war, the number of physicists interested in magnetism was limited, both because at that time there were few theoretical physicists in the world, and because there were many different fields in which quantum mechanics could be applied. So I seldom ran into problems of duplicating the work of other physicists, except for the calculations with the rotating dipole I mentioned near the beginning of my talk, and some duplication with Kronig on paramagnetic relaxation. As an example of the rather relaxed rate of development I might mention that while the first successful experiments on adiabatic demagnetization were made by Giauque at California in 1935 (Giauque and MacDougall, 1935), the first attempt to interpret these experiments in the light of crystal field theory was not until Purcell and Hebb published an article in 1937 (Purcell and Hebb, 1937) which was essentially a term paper in my course in magnetism which had only two students.

Shortly after the war, the whole tempo of research in magnetism changed abruptly. The development of radar in the war created apparatus and instruments for microwave spectroscopy, permitting exploration of a low-frequency spectral region previously practically untouched. Also infrared and optical spectroscopy of solids was pursued much more vigorously, with improved apparatus. On the theoretical side, crystalline and ligand field calculations were made in various centers, notably in Japan, going into much more detail and lengthy computation than in the work of my group at Wisconsin in the 1930s.

For the rare earths the prewar period may be described as the era of the rare-earth sulphate octohydrates, as the meager magnetic measurements at that time were mainly on these compounds. These materials are particularly annoying as they have a very complicated crystal structure, with eight rare-earth ions in the unit cell. However, the x-ray analysis (Zachariasen, 1935) that yielded this disconcerting information had not been made at the time of Penney and Schlapp's

work, and so they obtained the theoretical curve shown in Fig. 3, by making *faut de mieux* the simplifying assumption that the local crystalline field had cubic symmetry, and was the same for all the paramagnetic ions. Undoubtedly the local potential is more complicated. Even today there has been no attempt to reevaluate the crystalline field parameters for the sulphate octohydrates, both because of theoretical complexity and because of the paucity of new experimental data.

The most comprehensive crystalline field analysis for rare-earth salts in modern times is on the ethyl sulphates ( $\text{Re}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ ), which have only one ion in the unit cell and are magnetically dilute. One important result is that the higher-order harmonics in the series development of the crystalline potential are much more important than one thought in the early days. These ethyl sulphates have hexagonal symmetry. Were only second-order terms important, the crystalline potential would be of the simple type (7a), but actually there are also important terms involving fourth- and sixth-order harmonics, including those of the type  $(x \pm iy)^6$ . One sometimes worries how meaningful and reliable are the crystalline field parameters deduced from spectroscopic data, but very comforting magnetic measurements have been published by Cooke and collaborators (Cooke *et al.*, 1965). They measured the susceptibility both parallel and perpendicular to the hexagonal axis, and as shown in Fig. 6 found that the experimental results agreed exceedingly well with the theoretical curve calculated with the spectroscopically determined (Erath, 1961) crystalline field parameters.

One of the spectacular developments associated with spectroscopy of the solid state was the first optical laser constructed by Maiman (1960). By a sheer coincidence it involved transitions between the same ruby energy levels that were interpreted in terms of crystal field theory by Finkelstein and myself<sup>3</sup> in 1940. Cynics can well claim that our theoretical labeling of the energy levels was no more germane to the successful instrumentation of a laser than the prior naming of a star was to astrophysical studies thereof. Still it may be true that any theoretical understanding of the nature and relaxation rates of the different energy levels in solids may help the experimentalists a little.

Particularly gratifying to me were the improved determinations of spin-lattice relaxation times made at various laboratories. (See especially Scott and Jeffries, 1962; Ruby *et al.*, 1962.) These confirmed the reality of the bottleneck effect. They also verified the proportionality of the relaxation time in a certain temperature range to  $T^{-9}$  which I had predicted for salts with Kramers degeneracy and of sufficient magnetic dilution that there is no bottleneck.

The year 1946 brought about the discovery of nuclear magnetic resonance independently by Purcell, Torrey, and Pound (1946), and by Bloch, Hansen, and Packard

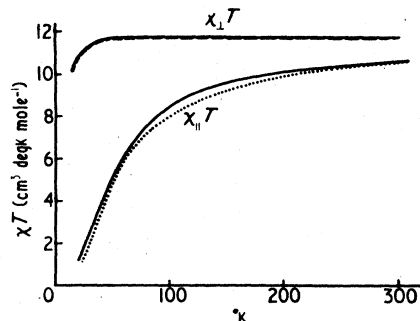


FIG. 6. The product of susceptibility times temperature for erbium ethyl sulphate as a function of temperature for directions parallel and perpendicular to the hexagonal axis. The broken curves represent experimental measurements of the susceptibility by Cooke, Lazenby, and Leask (1965); the solid curves are calculated theoretically with the crystalline field parameters of Erath (1961).

(1946). I need not tell you how enormously important the field of nuclear magnetism has become both for its basic scientific interest and its surprising technological applications. The nuclear magnetic resonance spectrometer has become a standard tool for any laboratory concerned with analytical chemistry, completely usurping the role of the Bunsen burner in earlier days. Measurements of transferred hyperfine structure give a quantitative measure of incipient covalence in molecular orbital or ligand field theory. Little of my own research has been concerned with nuclear magnetism, but in 1948 Purcell asked me if I could explain theoretically the size of the linewidths he and Pake were observing (Pake and Purcell, 1948, 1949; see also Bloembergen *et al.*, 1948) in the resonance of the F nucleus in  $\text{CaF}_2$ . It occurred to me that this could be done by applying the method of moments that Waller (1932) developed. The predicted magnitude of the mean square linebreadth and its dependence on direction agreed on the whole very well with experiment. The only difference in this calculation (Van Vleck, 1948) of the mean square dipolar broadening as compared with that originally performed by Waller is that he was concerned with the width in a weak magnetic field, whereas in the experiments by Pake and Purcell the dipolar energy is small compared to the Zeeman energy, and this necessitates the truncation of the Hamiltonian function, i.e., the omission of certain terms. A year previously I had also used Waller's method of moments in connection with explaining some apparently anomalous line shapes in some of the Leiden experiments on paramagnetic dispersion. Gorter was a visiting Professor at Harvard in 1947, and one morning we came to the laboratory and discovered that we had both overnight come to the conclusion that the explanation is to be found in an effect now generally known as exchange narrowing. Gorter had reached this conclusion on the basis of an intuitive picture, that the spin waves associated with exchange spoiled the coherence of the dipolar coupling, analogous to the motional narrowing discussed by Bloembergen, Purcell, and Pound (1948) in connection with nuclear magnetic resonance in liquids. On the other hand I used a more mathematical approach, showing that exchange enhanced the fourth but not the second

<sup>3</sup>Finkelstein and Van Vleck, 1940; Van Vleck, 1940c. These papers relate to chrome alum, whereas Maiman used chromium embedded in  $\text{Al}_2\text{O}_3$ , but the spectroscopic properties of the chromium ion are similar in the two cases; cf. p. 238 of Ballhausen (1962).

moment, thereby narrowing the line. The result was a joint paper by Gorter and myself (Gorter and Van Vleck, 1947; also Van Vleck, 1948).

So far I have not said much about ferromagnetism, partly because more of my own work has been in paramagnetism, but mainly because most ferromagnetic metals are very complicated since they are conductors. Over the years there have been arguments *ad infinitum* as to which is the best model to use, each researcher often pushing his own views with the ardor of a religious zealot.<sup>4</sup> Heisenberg's original model (1928) was one in which the spins responsible for the ferromagnetism did not wander from atom to atom, whereas in the band picture developed by Stoner (1936, 1938, 1939) the electrons carrying a free spin can wander freely through the metal without any correlation in their relative positions, as the exchange effects are approximated by an uncorrelated molecular field. Undoubtedly the truth is between the two extremes, and I have always favored as a first approximation a sort of compromise model, which may be called that of minimum polarity, (Van Vleck, 1953; also 1966). In nickel for instance, there is with this model continual interchange of electrons between the configurations  $d^{10}$  and  $d^9$  but no admixture of  $d^8$ ,  $d^7$ , etc. as then the correlation energy is increased.

Neutron diffraction is a very powerful new tool for disclosing how atomic magnets are arranged relative to each other. It has led to the surprising and spectacular discovery that in certain materials, notably rare-earth metals, the elementary magnets are arranged in a spiral, conical, or wavy fashion, rather than pointing all in the same direction within an elementary domain.<sup>5</sup> They can be ferromagnetic in one temperature region and antiferromagnetic in another. This weird kind of magnetism is sometimes called helical magnetism. Most rare-earth metals belong to this category and the mathematical interpretation of the experimental results is complicated and difficult despite the fact that the  $4f$  electrons participate but little in electrical conductivity, unlike the  $3d$  electrons in iron or nickel. I have not been involved in any of the theoretical analysis except for a point connected with the magnetic anisotropy. When I attended the conference on quantum chemistry sponsored by Professor Lowdin in Florida in 1971, Bozorth presented some measurements of the ferromagnetic anisotropy of Ho-Er alloys. He found that the anisotropy of pure holmium was approximately the negative of that of erbium, and vanished when there was an equal amount of Ho and Er, as shown in Fig. 7. It finally occurred to me that precisely the same property of spherical harmonics that explained the inversion of Fig. 4 in passing from  $\text{Co}^{++}$  to  $\text{Ni}^{++}$  also explained (Bozorth, Clark, and Van Vleck, 1972) the inversion of the anisotropy of Ho as compared to Er, with the obvious corollary that the Ho and Er contributions should cancel each other out for a 50% mixture. So sometimes primitive theory can still be useful, but in general a

<sup>4</sup>For a very complete review of all the different models and their limitations see Herring (1966).

<sup>5</sup>For an excellent discussion of the theory of the magnetic ordering in rare-earth metals see Elliott (1966).

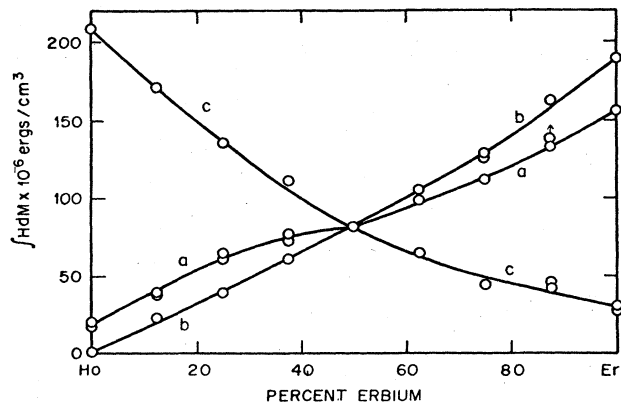


FIG. 7. The energy of magnetization for various amounts of Ho relative to Er. The three curves are for three different directions and would coincide were there no magnetic anisotropy. The latter is measured by the differences between the ordinates of the three curves.

higher degree of mathematical sophistication is required as time progresses, and as more and more exotic magnetic phenomena are discovered by the experimentalists. This you will learn from the addresses by Anderson and Sir Nevill Mott, but one can still say that quantum mechanics is the key to understanding magnetism. When one enters the first room with this key there are unexpected rooms beyond, but it is always the master key that unlocks each door.

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