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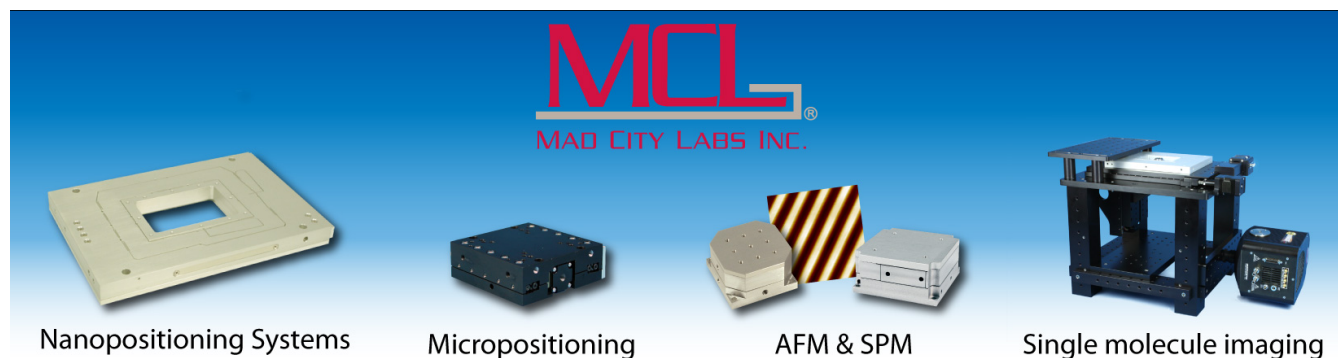
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Why is iron magnetic?

The long-sought explanation of the origin of ferromagnetism, which involves interactions both among the bound electrons and between bound and itinerant electrons, will guide the search for new magnetic alloys.

Mary Beth Stearns

The unravelling of the origin of magnetism in iron, cobalt, nickel and their alloys has been a fascinating subject of study for many years. It is elusive because the structure of the valence electrons in the transition metals is very complex. Only in the last decade has there been a sufficient understanding of this structure to appreciate the crucial features of ferromagnetism. We now know the two conditions the electronic structure of a metal must satisfy for it to be a ferromagnet, and this understanding is helping us synthesize new magnetic alloys.

In the 3d transition metals the valence electrons are of two types: 4sp conduction electrons—also known as “itinerant” electrons or just s electrons—and the 3d electrons. It is the character and interactions of these d electrons that is the key to understanding ferromagnetism. As is well known from quantum mechanics, the valence electrons have no separate identities but only probability densities of being in various states; reference to s or d electrons is meant in that sense. Furthermore, because solids do not have spherical symmetry, the classification of the valence electrons into different orbital symmetries is no longer completely valid. However, these classifications are still quite meaningful and are commonly used. Deviations from them are represented as “hybridization” or “admixing” of states.

Fortunately, one aspect of the magnetic behavior of iron and other 3d elements is especially simple: Because the d electrons are on the outer edges of the atom, their orbital angular momentum is effectively quenched by the crystal fields.

Thus the 3d elements, in contrast with the rare earths, have magnetic moments that are essentially due to only their electronic spins. Free atoms of many elements are known to have unpaired spins, and this is well understood. This phenomenon, of the stable state being that of maximum possible spin, follows directly from quantum mechanics and the Pauli exclusion principle, and is known as Hund's rule. However, in metals it is not quite as common for atoms to develop unpaired spins or moments. So essentially two questions arise in explaining ferromagnetism:

- ▶ Why and how do the individual atoms develop moments?
- ▶ Why do all these moments line up?

First approaches

Since the early days of quantum mechanics (around 1930) there have been two basic approaches to this problem; Conyers Herring's comprehensive review¹ covers the work done up to 1966. The first model was based on the work of Werner Heisenberg and Hans Bethe. It assumed that the d electrons were all *localized* (d_l), that is, strongly attached to individual atoms, and the spins were aligned because the energy of the system was lowered by the *direct-exchange interaction* between adjacent atoms with parallel spins. This was kind of an interatomic Hund's-rule interaction. However, the wave functions were not well known at that time, so this proposed model was qualitative rather than quantitative.

Moreover, several experimental facts conflicted with such a simplistic approach. The most compelling were:

- ▶ The moments of Fe, Co and Ni are not integers; they are 2.2, 1.7 and 0.6, Bohr magnetons respectively.

▶ The values of the low-temperature specific heat of Fe, Co and Ni are too high to be caused by the number of s-like electrons known to be present, suggesting the presence of other conduction electrons.

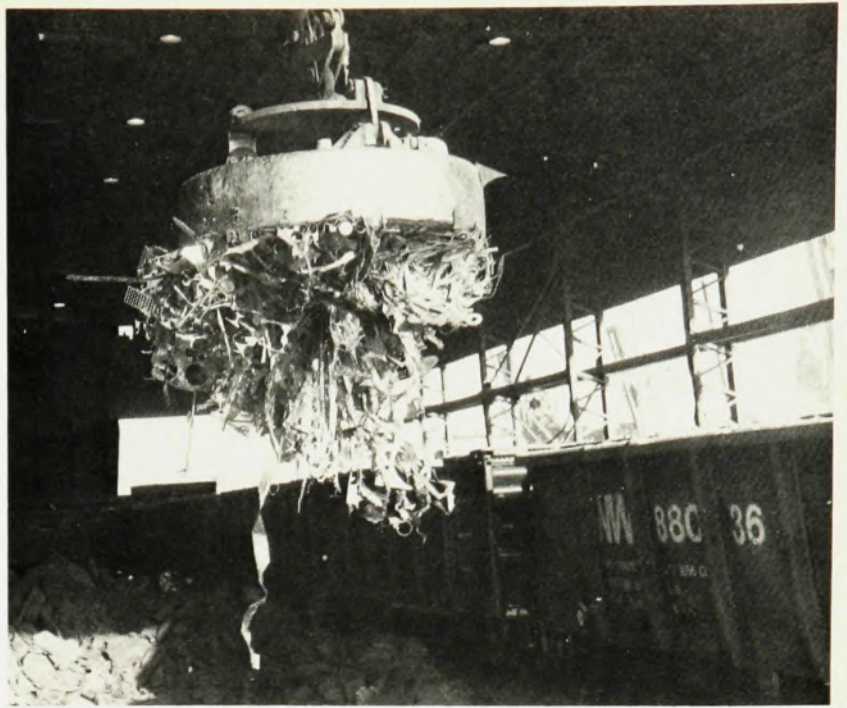
In 1960 this purely localized model was more conclusively disproven by R. Stuart and Walter Marshall, who made a computer calculation of the direct exchange between localized London-Heitler 3d wave functions. It showed that this interaction was much too small to account for the ferromagnetism of iron. Various similar calculations since then have all come to the same conclusions.

The second approach, also proposed in the early 1930's and pursued by Felix Bloch, Ya. I. Frenkel, Edmund Stoner and many others over the years, assumed that all the valence electrons, both 4sp and 3d, are itinerant; that is, they are able to move freely through the lattice. This formulation unfortunately is so intractable that no practical quantitative calculations have resulted from it.

Much experimental evidence also appeared against the all-itinerant model. The most direct is:

- ▶ The entropy associated with the transition, through the Curie temperature, from the magnetic to the non-magnetic state, indicates that Fe and Ni have degrees of freedom due to local moments.
- ▶ Measurements of the magnetic form factor show that the magnetic electrons have spatial distributions very similar to those of free atoms.
- ▶ Magnetic moments still exist above the Curie temperature and are nearly the same as the low-temperature saturation moments.
- ▶ The electron structure is observed to be essentially unchanged above and below the Curie temperature, although it should

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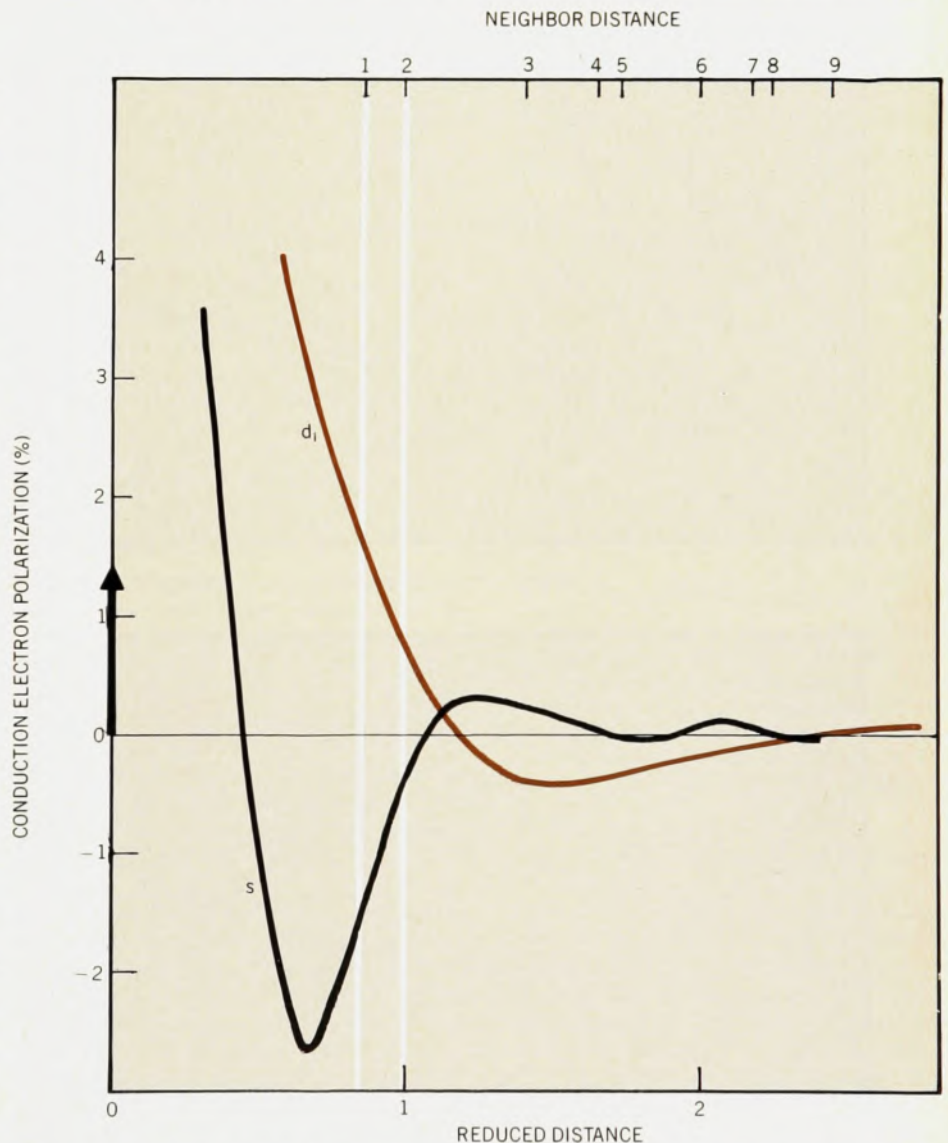


be different in an itinerant model.

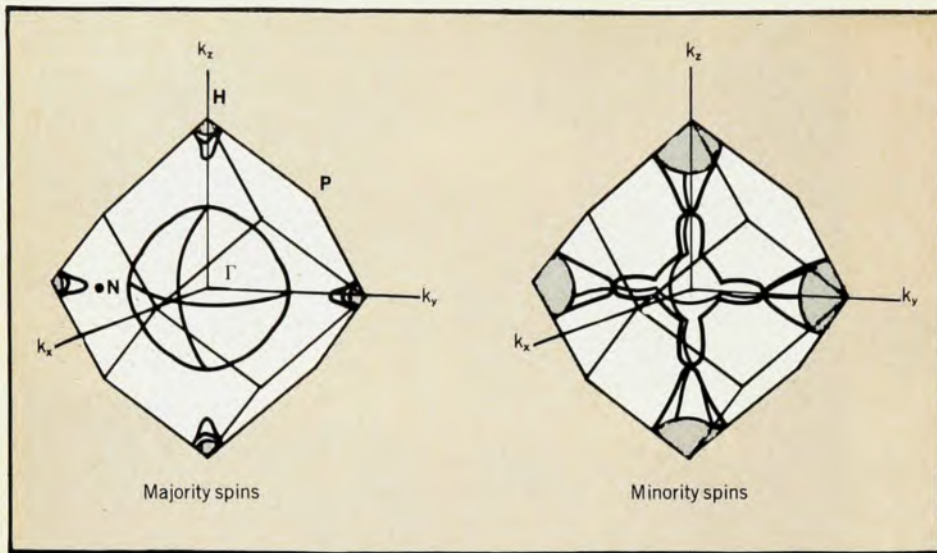
The experimental situation can be summarized by noting that experiments that mainly probe features close in to the nucleus, such as neutron scattering and hyperfine fields, mostly measure the localized electrons, while those that measure the tails of wave functions, such as transport-property measurements, mostly see the itinerant electrons.

Inevitably, much discussion in recent years has been concerned with whether or not the two descriptions were equivalent. Because mathematically the ultimate in localization, the delta function, can be expressed in terms of completely itinerant functions, sines and cosines, from an extreme point of view there is no difference. However, there is little physical insight to be gained by a purely mathematical formulation, especially if the problem is so complex that it is intractable, as in this case. Because physics is an experimentally based field, it is often more fruitful to use concepts corresponding closely to reality; the problem can then be formulated in a manner more sharply focussed on the dominant interactions. Therefore my approach is that it is meaningful and worthwhile to retain both the concepts of locality and itinerancy. Below I shall define and identify these concepts more specifically.

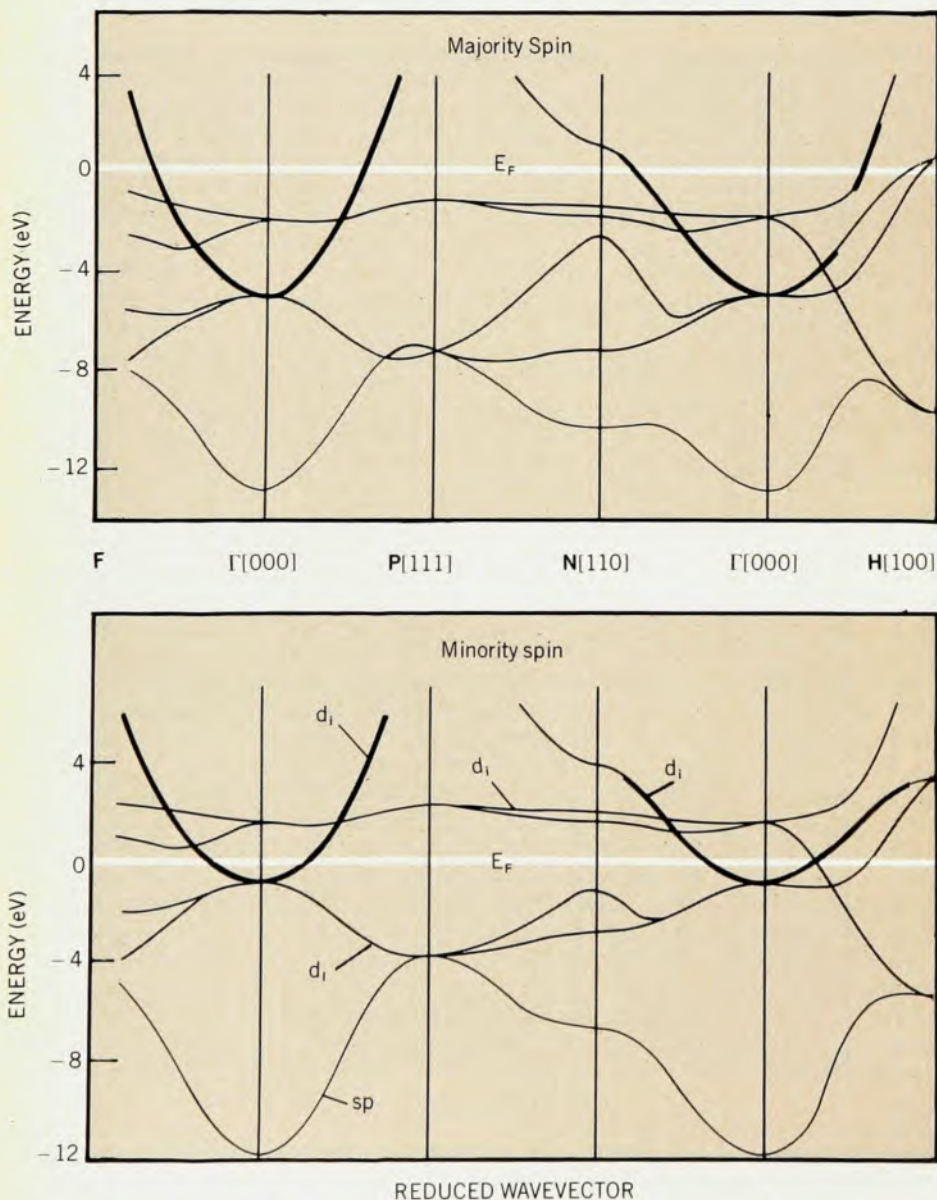
In the early 1950's Clarence Zener proposed a somewhat different model incorporating both local and itinerant features. He assumed that the d electrons were localized and that they polarized the s-like conduction electrons, which then aligned the atomic spins. He envisioned these itinerant electrons as being uniformly and positively polarized. (Positive here means in the same direction as that of the localized d_i electrons.) However, it was soon realized by others²



Distance variation, in units of lattice constant, of conduction-electron polarization in iron. The arrow represents the spin of the localized d electrons. The black curve shows the *measured* polarization of the 4s-like conduction electrons, negative for the first two neighbors; the colored curve, the *hypothetical* polarization of the d-like conduction electrons—for ferromagnetic coupling, the first node of this curve must be beyond the nearest neighbor. Figure 1



The Fermi surface of iron, obtained from de Haas-van Alphen measurements. The electron and hole pockets along the k_x axis as well as the cylindrical surfaces between H and N have been left out for clarity. From A. V. Gold and co-workers, reference 4. Figure 2



The band structure of iron, showing the dependence of the spin-up (majority) and spin-down (minority) band energies on wavevector. From K. J. Duff and T. P. Das, ref. 6. Figure 3

that the s - d_i exchange polarization would give rise to an oscillatory spatial polarization of the conduction electrons, which falls off rapidly with distance from the localized moment, as shown in figure 1. These conduction electron polarizations are now referred to as the RKKY (Ruderman-Kittel-Kasuya-Yosida) oscillations or Friedel oscillations. In 1960, after the purely localized model was shown to be too weak to cause ferromagnetism, the RKKY theory of the s - d_i interaction became the favored explanation.

Conduction-electron polarization

In the early 1960's it became possible to measure the s -like polarization with Mössbauer and nuclear magnetic resonance techniques. Due to the quenched orbital contributions in iron, cobalt and nickel, such experiments measure mainly those electrons at the nucleus, that is, the s -like electrons. By using dilute iron alloys containing solutes that look like magnetic holes, aluminum and silicon, I showed³ that it was possible to observe the effect of a missing iron atom's magnetic moment on the nearby iron atoms. The spectra of these nearby Fe atoms had structure due to the polarization of the s electrons, and therefore these spectra could be analyzed to give the polarization contributions for the first few shells of neighboring atoms.

The important result from these experiments was that the s -electron polarization was negative at the first two neighbor shells, as shown in figure 1. Thus, the polarization of the s electrons at the distance of the first nearest neighbor from an iron atom is in the opposite direction of that of the atom itself. This tends to align the Fe atoms antiferromagnetically.

Because both direct interactions between localized d_i electrons and coupling through s -like electrons had now been ruled out as causing ferromagnetism, I proposed³ that the coupling of the d_i electrons was through a small number of itinerant d_i electrons. RKKY theory shows that the negative polarization of the s -like electrons at first-nearest-neighbor distances occurs because there are too many $4s$ electrons in iron, about one per atom. The form of the conduction-electron polarization around a local moment is a function of $\cos 2k_F r$ and $\sin 2k_F r$, where k_F is the wavevector at the Fermi surface. The first node therefore occurs at $k_F r = \text{some constant}$. Because k_F depends on the number of conduction electrons, if k_F and hence the number of conduction electrons is too large, r is small, and the first node occurs at a distance closer than the nearest neighboring atom. Properly modified, RKKY theory is also applicable to the d_i conduction electrons. It thus is a simple matter to estimate how few d_i electrons must be present for ferromagnetic coupling: This

condition is that the first node be beyond the first-nearest-neighbor distance.

An upper limit to the number of d_i electrons obtained in this manner from RKKY theory is about 0.4 d_i electrons per atom. Thus, at most about 5% of the d electrons can be itinerant in Fe, Co and Ni. Because d_i electrons have an orbital symmetry very similar to that of the d_j electrons, the d_i - d_j Coulomb exchange interaction is considerably stronger than the s - d_j interaction, causing Fe, Co and Ni to be ferromagnetic. Knowing how many d_i electrons to expect, I then set out to look for more direct evidence for the number of d_i electrons. As usual, when the correct question is asked, the answer is easy to find.

Itinerant d_i 's: only a few

The most direct evidence that the number of itinerant d electrons is small comes from three sources, de Haas-Van Alphen and spin-polarization measurements, and band-structure calculations.

In *de Haas-van Alphen experiments*,⁴ this effect measures the shape and size of the Fermi surface (the boundary in wavevector space between the filled and empty conduction-electron states). Thus, these experiments give a measure of the number of conduction electrons. Figure 2 shows the Fermi surfaces for the majority and minority spins obtained for iron. The electron and hole pockets along the k_x axis and the cylindrical surfaces between points H and N have been left out for clarity. Although the central sphere-like surfaces were originally identified as s -like, it is now clear that they are the d_i electrons. The s electrons are essentially unpolarized while these surfaces indicate about 90% polarization. The measured k_F values correspond to 0.2 \uparrow electrons and 0.01 \downarrow electrons, in excellent agreement with the condition of keeping the polarization node of the d conduction electrons out far enough to give ferromagnetic coupling.

Recent *spin-polarization measurements*⁵ from tunnelling between ferromagnetics and superconducting aluminum, separated by an oxide layer, further confirm the smallness of the number of d_i electrons. These experiments measure mainly the highly mobile electrons within 1 meV of the Fermi surface. As can be seen from figure 3, these are essentially the d_i electrons; there are very few s -like electrons at the Fermi surface. There is much evidence from other types of experiments that the s electrons have very little polarization, whereas the measured tunnelling polarizations are high (in iron it is about 44%) and in excellent agreement with the degree of polarization of the d_i electrons at the Fermi surfaces for Fe, Co and Ni and its alloys.

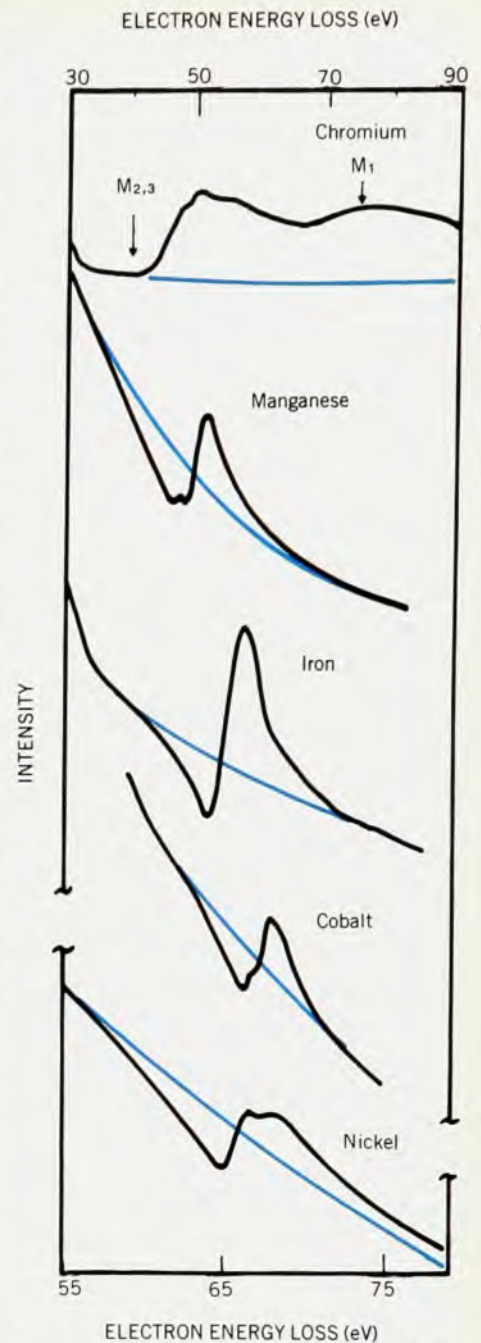
Band-structure calculations presumably should give a realistic description of the character of the outer valence electrons, but they have frequently been

looked upon as in a developmental stage, with their accuracy and interpretation in doubt. It is therefore gratifying to see that these calculations showed just the feature sought. Figure 3 shows the results of a typical band-structure calculation⁶ for iron. The graphs show the spin-up (majority) and spin-down (minority) band energies as a function of wavevector k . In a band picture, the localized electrons are represented by somewhat flat bands and the itinerant electrons by parabolic bands, because $E \approx \hbar^2 k^2 / 2m_e^*$, where m_e^* is the effective mass.

In figure 3 we indeed see this behavior. The Fermi energy E_F is taken as zero. Consider the bands near the center, Γ , of the Brillouin zone (the unit cell in k space). There the lowest state, at $E \approx -12$ eV is due to the s -like conduction electrons; it is parabolic around Γ . The higher five states are d states. For each spin, four of the states are seen to be quite flat near Γ , while one, shown darkened in the figure, is parabolic. Proceeding out from Γ along the [110] direction toward N, or in the [111] direction toward P, we see that four of the bands remain quite flat. The mild curvature that these bands develop can be attributed to hybridization between the s and d_j bands. The parabolic d bands, shown as heavier lines in the figure, correspond to the itinerant d_i electrons. These bands are seen to cross the Fermi level E_F in the F, P and N directions (from Γ) with essentially no hybridization with the s -like electrons and have a curvature corresponding to that of the free-electron mass. From their k values at the Fermi level we can estimate the number of d_i electrons. We find 0.3 \uparrow and 0.05 \downarrow electrons, in reasonable agreement with the de Haas-van Alphen measurements in figure 2.

Intra-atomic exchange criterion

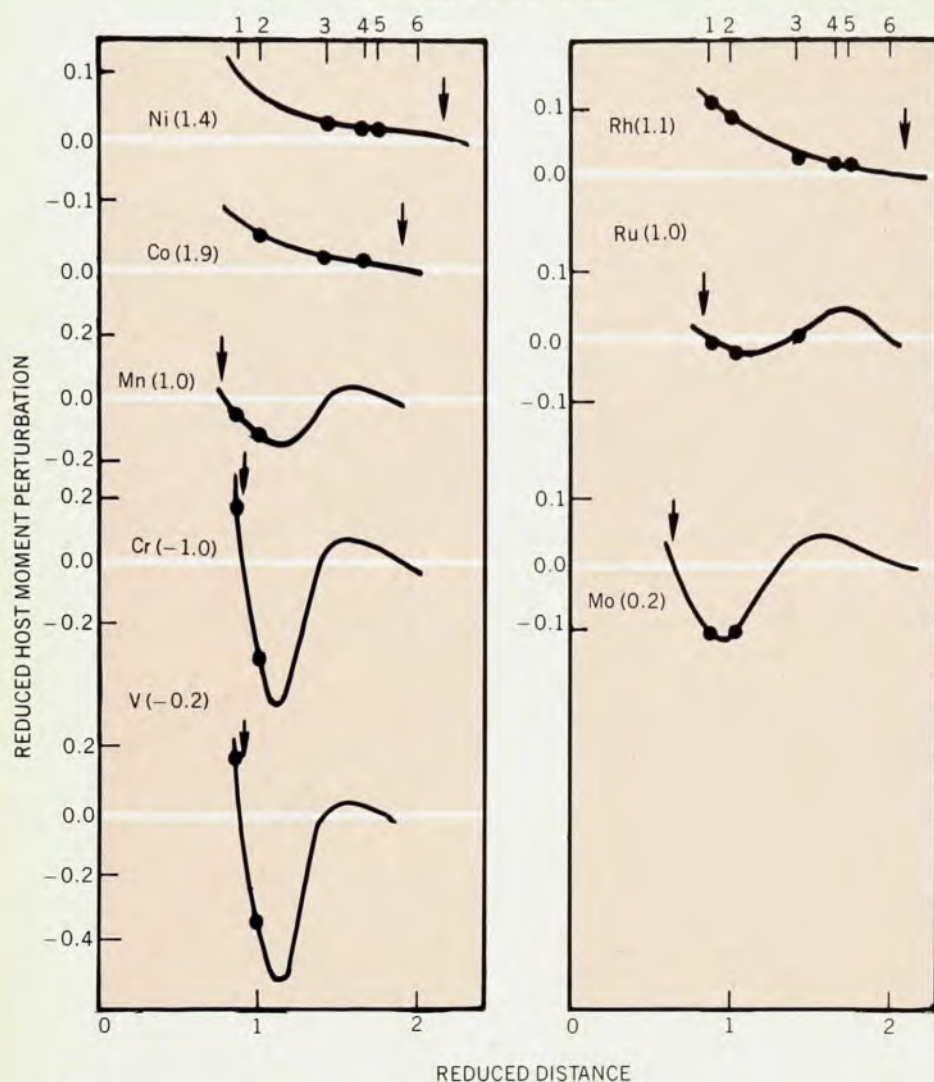
The classification into d_i or d_j electrons can now be made more quantitative. A pair of localized electrons having the same spin direction are lower in energy than a pair with opposite spin directions by an amount called the intra-atomic exchange energy U . This is about 1.5 eV per spin for the 3d elements.⁷ Thus, the natural criterion for the localization of a single band is that its width be less than or about equal to U . Under this condition, some electrons stay on an atom long enough to interact and align their spins, so that the atom obtains a moment. Band calculations for iron give a bandwidth (energy spread in the Brillouin zone) for the upper two d bands of about 0.7 eV, so they indeed meet this criterion. However, this condition concerns only the *formation* of local moments. For ferromagnetism to occur, there is the added condition that the d_i electrons present must be few enough to allow the alignment of these moments. As can be seen in figure 3, the itinerant electrons have bandwidths much



Typical transmission spectrum for energy loss in single crystals due to the $3p \rightarrow 3d$ transitions. (Note changed energy scale for nickel.) The colored curves depict the smooth background extrapolated from the far regions. Arrows indicate the expected positions of the $3p \rightarrow 3d$ ($M_{2,3}$) and $3s \rightarrow 3d$ (M_1) transitions. Figure 4

larger than U . For the s and d_j electrons these widths are about 10 eV.

Such a picture also easily explains the magnetic behavior of all the 3d transition elements and their alloys. At the beginning of the 3d series, the atomic number is low enough that all the d electrons are very loosely bound, so they are all itinerant. As the series is crossed, and the atomic number increases, some of the 3d electrons become more tightly bound and their bandwidths decrease. It is well established that through chromium all the outer electrons are itinerant. (The magnetic state of Cr represents a much



Perturbations of the magnetic moment of iron host atoms surrounding an atom of a transition-metal solute, as a function of the distance from the solute atom. The numbers give the moment of the solute in iron, in Bohr magnetons; the arrows point to nodes. Figure 5

more exotic type of magnetism than the ferromagnetism we are considering here. It is a rather special spin-density-wave ground state of the conduction electrons, which is incommensurate with the lattice, arising from an unusual Fermi surface configuration. Specific-heat measurements show that there are no localized moments present in chromium.⁸

The first element of the 3d series with some localized d electrons is manganese. However, as might be expected, Mn still has too many itinerant d electrons and therefore exhibits antiferromagnetism. Iron is the first 3d element to have few enough d_i electrons to meet the criterion for ferromagnetism. Cobalt and nickel, with even fewer d_i , in this sense are "better" ferromagnets than iron; this shows up in their alloying behavior. For example, Ni, when alloyed with a 3d element to its left in the periodic table, such as Cr, remains ferromagnetic for larger additions of Cr than does Fe. This is because the ferromagnetism is determined by a weighted average of the number of d_i

electrons. Thus, the average-moment behavior of the 3d alloys (Slater-Pauling curve) follows naturally from this model.

The formation of localized states in crossing the 3d series can be clearly seen in the lineshapes of the $3p \rightarrow 3d$ transitions ($M_{2,3}$) of these elements. The lineshapes resulting from the promotion of an electron from the 3p level (at about 50 eV below E_F) to the empty 3d levels above E_F have been measured by x-ray absorption and electron-energy-loss experiments and the latter results⁷ are shown graphically in figure 4.

The lineshape of chromium is seen to be very different from those of manganese through nickel; it is characteristic of the onset of an empty conduction or itinerant band. In contrast, the lineshapes of Mn through Ni have an antiresonance (or Fano) lineshape, consisting of a negative dip and a positive peak. Such a lineshape is typical of a localized level when there is interference of the localized state with a continuum background. In this case the

background is due to electronic transitions from 3d states to higher f states.

Shape of the d polarization

Unfortunately, there is no method to measure the d conduction-electron polarization as directly as the s polarization is measured from hyperfine fields. However, the wave functions of the d_i electrons, when well inside an atom, are very atomic-like, and so the d_i electrons do manifest their polarization as small contributions to the atoms' magnetic moment. Thus, when a foreign transition element is substituted into a ferromagnetic host, a direct indication of the polarization perturbations caused by the solute's d conduction electrons is given by the small moment perturbations on the nearby host atoms. These perturbations have been obtained from two types of experiments:

► The analysis of hyperfine field spectra and magnetization-saturation data of transition-metal solutes in Fe give the perturbations of Fe atoms surrounding the solute atom.⁹

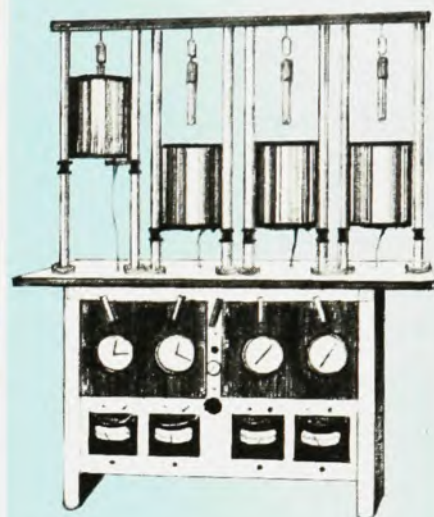
► Neutron cross sections as a function of wave vector, obtained from diffuse elastic scattering, give the Fourier inverses of the moment perturbations.¹⁰ The resulting moment perturbations obtained by the two methods are in good agreement; they are shown for an iron host in figure 5.

Because the moment perturbations in iron are closely related to the polarization of the d conduction electrons the feature that we expect to see is that the first node of this polarization moves in from large distances to the vicinity of the nearest-neighbor distance as the number of d_i electrons increases. This behavior is evident in figure 5, and is shown by the arrows that point to those nodes. Consistent with this picture of polarization behavior is the finding that the moments on chromium and vanadium are aligned antiferromagnetically; this is due to the large number of d_i electrons in their vicinity.

We have seen that two conditions must be satisfied to get ferromagnetism. These two conditions can be pictured conveniently as in figure 6. The first diagram in this figure represents a simplified d-band structure for a hypothetical "paramagnetic iron" (not ordinary iron above the Curie temperature), for which we assume that there are no intra-atomic Coulomb exchange interactions (no Hund's rule) and no Coulomb exchange interactions between the d_i and d_j electrons. The flat bands represent the d_i electrons; the parabolic band, the d_j electrons. In this case the Fermi level falls somewhere in the top two levels labelled E_g .

The first condition for ferromagnetism is that we have some localized electrons that develop a moment. Because we have assumed some of the d electrons are localized, this condition is met by turning

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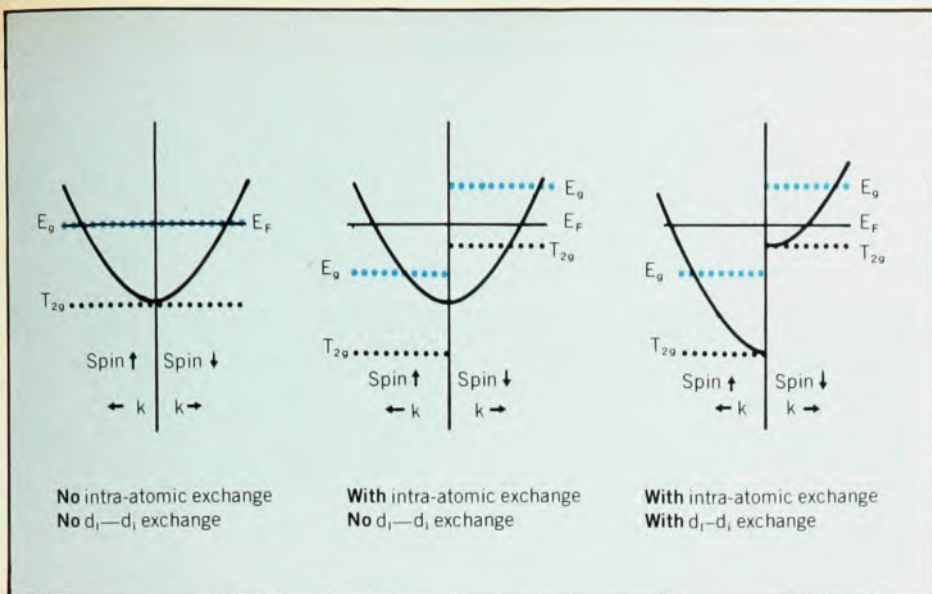
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Schematic representation of the interactions and conditions that give rise to ferromagnetism in iron. The detailed explanation of this figure is in the text. Figure 6

on the intra-atomic exchange interaction. This splits the localized spin-up and spin-down states and develops a localized moment, as shown in the middle diagram of the figure. The intra-atomic exchange interaction does not polarize the d_i electrons, as is evidenced by the fact that elements with only itinerant valence electrons (such as Cr, V, Ti, Sc and all the elements with sp valence electrons) do not develop moments. Local moments must be present to get ferromagnetism.

The second condition for ferromagnetism is met by turning on the d_i-d_j exchange interaction and having very few d_i electrons per atom. Turning on the d_i-d_j exchange polarizes the d_i electrons as shown on the right in figure 6. (Note that this diagram very closely resembles the actual band structure of Fe shown in figure 3. Compare, for example, the d bands from Γ to P in figure 3 with the \uparrow bands plotted to the left.) The number of d_i electrons determines the spatial distribution of the d_i -electron polarization and whether the local moments become ferromagnetically or antiferromagnetically coupled.

If there are different types of conduction electrons, those with the strongest polarization in the near-neighbor region determine the collective magnetic state. For ferromagnetism to appear, the number of conduction electrons must be low enough that the polarization remains positive in the near-neighbor region. In the 3d ferromagnets, the d_i-d_j Coulomb exchange interaction is considerably stronger than the s- d_i interaction and the polarization of the d_i conduction electrons dominate.

Alloys

Applying this model gives us great insight into magnetic-alloy behavior. The ability of the polarization of the d con-

duction electrons to determine the magnetic behavior can now be seen and controlled in many alloy series. The binary alloys of the transition elements are simple and classical examples of this type of behavior. Other, more complex, magnetic-alloy series, such as the Heusler alloys, alloys between rare earths and transition metals and actinide-series alloys, are also beginning to be understood from this point of view. This will lead to a greater ability to synthesize magnetic materials with specific desired properties.

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