

Magnetism

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The word *magnetism* covers the response to a magnetic field (paramagnetism, diamagnetism) and the magnetic ground state (ferromagnetism, antiferromagnetism). In everyday language, when we say a material is “magnetic”, we mean it has a magnetic ground state – usually ferromagnetism – but so-called non-magnetic materials can still have magnetic response to an external magnetic field. The terms *paramagnetism* and *diamagnetism* are usually used for materials with non-magnetic ground states.

The ground state is influenced by several mechanisms: exchange interaction, itinerant magnetism, topological magnetism. Above the ground state, we have magnetic excitations like spin waves.

1 Magnetic response of individual electrons

For local electrons, we have Curie’s law and Langevin diamagnetism (TODO: ref); for itinerant electrons, we have Pauli paramagnetism, Landau diamagnetism, and more (TODO: ref).

1.1 The magnetic moment

TODO: lecture on the Friday; Hund’s rule

1.2 Electromagnetic effective theory

TODO: χ, M

1.3 Paramagnetism of itinerant electrons

$$M = \mu_B(n_{\uparrow} - n_{\downarrow}) = \mu_B^2 B \rho(E_F), \quad (1)$$

1.4 Landau diamagnetism

We can see the magnitude of itinerant paramagnetism usually dominates that of Landau diamagnetism, and therefore most metals are paramagnetic. Transitional metals on the right of the periodic table, like silver, copper, and gold, however demonstrate diamagnetism. The explanation is nontrivial TODO

Generally all the magnetic responses are rather weak. We need very strong external magnetic field to make these phenomena mechanically significant. With a ~ 16 T magnetic field, the diamagnetism of water is obvious enough for us to trap a frog and let it levitate in the air. For superconductors however, since they repulse magnetic field completely (because electromagnetic modes inside a superconductor are gapped), magnetic levitation can be easily observed.

1.5 Van Vleck paramagnetism

2 Some easy-to-explain localized magnetic ground states

In this section we discuss systems in which electrons that contribute most to the magnetic ground state are localized around atoms, and therefore we can talk about magnetism of atoms. In this section we put the problem of domain walls aside: we assume a magnetic order is formed in the thermodynamic limit. TODO: are domain walls classical enough?

A **ferromagnetic** material is a material where the magnetic moments of all atoms are towards the same direction. It breaks the spin rotational symmetry. A **antiferromagnetic** material is a material where the material is broken into several sublattices, each of which are in

a ferromagnetic state, but the magnetic momenta among the sublattices cancel each other. It brakes both the spin rotational symmetry and the translational symmetry. A **ferrimagnetic** material is antiferromagnetic one with a non-zero overall magnetic moment. The states all have *long-range orders*: $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ doesn't come to zero even when the distance between the two spins goes to ∞ .

2.1 Direct interaction between magnetic moments

2.1.1 The magnetic dipole-dipole interaction

It can be proved that the dipole-dipole interaction energy is

$$E_{\text{dipole}} = \frac{\mu_0}{4\pi} \left(\frac{\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2}{r^3} - 3 \frac{(\boldsymbol{\mu}_1 \cdot \mathbf{r})(\boldsymbol{\mu}_2 \cdot \mathbf{r})}{r^5} \right). \quad (2)$$

An order of magnitude estimation tells us the energy is $\sim 1 \times 10^{-4}$ eV. We know the band energy is ~ 1 eV, and therefore (2) is too weak for a microscopic description of magnetism – and it can only leads to antiferromagnetism.

2.1.2 Spin-spin interaction caused by exchange interaction

There however exists another interaction channel that gives us a $\mathbf{S}_1 \cdot \mathbf{S}_2$ Hamiltonian. We know the eigenstates of the 2-electron system

$$H = \sum_{i=1,2} \left(\frac{\mathbf{p}_i^2}{2m} - \frac{Ze^2}{r_i} \right) + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \quad (3)$$

are the **bonding wave function** and the **anti-bonding wave function**: the former is symmetric and the latter is antisymmetric. Now (3) is only about the spatial part. We know Pauli exclusion principle requires the many-body wave function to be antisymmetric, and therefore the bonding wave function of the spatial part comes together with the antisymmetric spin wave function – the **singlet** subspace, and the anti-bonding wave function of the spatial part comes with the symmetric spin wave function – the **triplet** subspace. Thus, the energy difference between the bonding wave function and the anti-bonding wave function can be equivalently attributed to the spin orientation. If ψ^B is the ground state, then the spin configuration in the ground state is one-up-one-down.

In this mechanism, what's important is the Coulomb interaction between electrons localized around different atoms. Thus, even if the magnetic momentum of a *single* atom is strong, if the exchange interaction isn't strong enough, the ferromagnetism is still not stable enough. This is (at least qualitatively) demonstrated by experimental results: the Curie temperature seems to be largely independent of the magnetic momentum per atom.

Now we write an effective Hamiltonian between \mathbf{S}_1 and \mathbf{S}_2 . From $\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$, we know

$$2\mathbf{S}_1 \cdot \mathbf{S}_2 = s(s+1) - s_1(s_1+1) - s_2(s_2+1), \quad (4)$$

and the RHS is $-3/2$ for a singlet and $1/2$ for a triplet, and therefore we find

$$\frac{1}{2} + 2\mathbf{S}_1 \cdot \mathbf{S}_2 = \pm 1.$$

Now the total energy is $C_{12} \pm J_{12}$, and therefore we get

$$H = C_{12} \pm J_{12} = C_{12} - \frac{1}{2}J_{12} - 2J_{12}\mathbf{S}_1 \cdot \mathbf{S}_2. \quad (5)$$

So we arrive at the **Heisenberg Hamiltonian**. Some people will replace $2J_{12}$ by J_{12} : this is a frequent notational difference.

2.1.3 The Heisenberg model

The Heisenberg model is then

$$H = -2 \sum_{\langle i,j \rangle} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j. \quad (6)$$

At this point we only place magnetic moments on atoms; we ignore all itinerant electrons which have the possibility to be magnetic.

2.1.4 The Weiss molecular field model

(6) is generally hard to solve. One way to show that it models ferromagnetism is by mean-field theory. We do **Weiss molecular field model**: we assume that (6) is equivalent to a model with no spin-spin interaction, where what is felt by each spin is a mean-field

$$\mathbf{H}_{\text{total}} = \mathbf{H} + \mathbf{H}_M, \quad \mathbf{H}_M = \lambda_M \mathbf{M}, \quad (7)$$

where \mathbf{H} is the external magnetic field (which should be introduced by adding a $\mathbf{S} \cdot \mathbf{H}$ term in (6)), and we have

$$\lambda_M = \frac{2zJ_{ij}}{Ng^2\mu_B^2\hat{\mu}}, \quad (8)$$

where z is the number of nearest neighbors of each site. We then can obtain the relation between \mathbf{M} and $\mathbf{H}_{\text{total}}$ from Curie's law (Dresselhaus p. 40-43?)

$$\mathbf{M} = \left(\frac{Ng^2\mu_B^2(j+1)j\hat{\mu}}{3k_B T} \right) \mathbf{H}_{\text{total}}, \quad (9)$$

and we find

$$\mathbf{M} = \chi \mathbf{H}, \quad \chi = \frac{C}{T - C\lambda_M}. \quad (10)$$

Obviously, χ diverges when $T \rightarrow T_c^+$, where even when we add a very small external \mathbf{H} , we get a very huge \mathbf{M} – an indication that the system becomes ferromagnetic after T passes T_c .

It should be noted that since the response of \mathbf{M} to $\mathbf{H}_{\text{total}}$ is assumed to follow the high-temperature pattern, the mean-field solution shouldn't be expected to work *quantitatively* when T really approaches T_c . Indeed, T_c can be seen as a temperature scale that tells us how high is "high temperature", where the Curie law works quantitatively.

Another comment is the divergent behavior of χ doesn't rely on the exact form of the Hamiltonian: the only things the above calculation takes from (6) are z and J_{ij} , which decide the value of λ_M . It even isn't constrained to the field of magnetism. The same Curie-Weiss law-like behavior can be found in nematic susceptibility (stress-deformation), elastic moduli (stress-strain), electric susceptibility (polarization-electric field), charge susceptibility (charge number-chemical potential), and more.

\mathbf{H}_M can be very large, much larger than the strongest magnetic field created by deconstructive methods. A magnet doesn't explode, because \mathbf{H}_M is highly localized.

2.1.5 The origin of the anisotropy

Since the crystal lattice structure is not isotropic, we shouldn't expect J_{ij} to be isotropic. The question is how the lattice influences magnetism. The leading contribution is SOC. TODO: any model about this?

The anisotropic limit of the generalized Heisenberg model is the **Ising model**

$$H = - \sum_{\langle i,j \rangle} J_{ij} \sigma_i \sigma_j - \sum_j h_j \sigma_j. \quad (11)$$

That's to say, only z -axis spins are actively engaging in magnetism. Treatment of the Ising model is much easier, because now at least we don't need to consider vector spin degrees of freedoms, but still it's hard. Mean-field solutions are shown in textbooks, but they predict wrong T_c 's and in the 1D case, falsely report that there is a phase transition while the exact solution of the model tells us it doesn't. The problem here is again universally seen in all mean-field methods: fluctuation is not completely taken into account. We do have a phase transition in 2D, because now a spin has more neighbors, and the energy cost to have a \downarrow -spin in a sea of \uparrow -spins is high, so neglecting thermal fluctuation is more acceptable.

2.2 Ferromagnetic systems

2.2.1 Magnetic domains

In a ferromagnetic system we have magnetic domains, in each of which spins go in the same direction but the magnetic moments of two neighbor magnet domains are opposite to each other.

The main reason of this is the competition between the long-range magnetic dipole interaction (Section 2.1.1) and the short-range exchange interaction: the short-range interaction sorts the spins in a small region into one direction, forming a large total magnetic moment, while the long-range magnetic dipole interaction instructs these average magnetic moments to have staggering orientations. The directions of magnetic domains around the boundary is usually parallel to the boundary, TODO: easy axis, minimize $-\mu_0 \mathbf{M} \cdot \mathbf{H}$

If we break a magnet, usually we will cut through many existing magnetic domains. The broken domains immediately realign to minimize $-\mu_0 \mathbf{M} \cdot \mathbf{H}$ and now have orientations parallel to the boundary. So now the attraction force across the cut is too weak to glue the two parts together into one magnet.

The energy of a domain wall is

$$\sigma_W = \underbrace{\frac{JS^2\pi^2}{Na^2}}_{\text{exchange}} + \underbrace{KNa}_{\text{magneto-crystalline anisotropy ??? TODO}}. \quad (12)$$

Here the magneto-crystalline anisotropy term comes again from SOC: since there is anisotropy in the crystal structure, due to SOC, magnetic moments have preferred directions.

2.2.2 M-H hysteresis

Even when we already reach the transitional temperature, it's still possible for a ferromagnetic system to have zero \mathbf{M} , because the directions of magnetic domains are staggering.

One thing to keep in mind is \mathbf{M} is not the only relevant degree of freedom for a macroscopic theory of a magnet: the structure of internal magnetic domains is also important. This means if we choose to use \mathbf{M} and \mathbf{H} only to describe a magnet, the relation between the two depends on the history. TODO: more thought on this: is magnetic domains really necessary for the curve?? Since it seems Landau's theory is already enough

TODO: figure 1.30.1

According to the shape of the magnetic hysteresis, we can classify magnets into **soft** and **hard** magnets. A hard magnet has very steep \mathbf{M} - \mathbf{H} relation: when the external field is not strong, no magnetization happens, and when \mathbf{H} exceeds a certain point, all of a sudden, a very strong magnetization occurs.

TODO: what an exchange bias?

When we zoom in the \mathbf{M} - \mathbf{H} curve, we can find small steps with random height. This is called the **Barkhausen effect**. This is believed to be an effect involving defects: TODO: fig. 1.30.2 This is a main source of noise in the magnetic recording tape.

2.3 Antiferromagnetic systems

2.3.1 Direction of \mathbf{H} and susceptibility

To gain a response of \mathbf{M} – instead of the antiferromagnetic order parameter – it's more convenient to apply an external field perpendicular to the molecular magnet moments. TODO: fig. 1.30.3 This has already been demonstrated experimentally: below the antiferromagnetic transition temperature, when \mathbf{H} is parallel to the direction of molecular magnetic moments, as T goes down, χ dramatically decreases, but when \mathbf{H} is perpendicular to molecular magnetic moments, χ almost doesn't change. TODO: 1.30.3

2.3.2 Domain walls

2.4 Exchange energy induced by itinerant electrons

For any type of fermions, the larger the box is, the lower the energy can be. That's to say, hopping can help to reduce the energy. TODO: quantitatively argument This is the underlying mechanism for indirect exchange and super- and double-exchange.

2.4.1 Superexchange

Antiferromagnetic in MnO is confusing: the distance between Mn^{2+} ions is too large for direct exchange. The magnetic interaction therefore has to come from another mechanism.

The general idea is electrons tend to be delocalized to reduce Coulomb energy: if they are

Superexchange is present in a simple system in which only nearest neighbor hopping is important and the role of Coulomb interaction is limited to on-site repulsion. We know it's possible to integrate out hopping electrons in the half-filled Hubbard model to get a Heisenberg model. This is a semi-quantitative demonstration of superexchange.

2.4.2 Double exchange

In a material we have Mn^{3+} and Mn^{4+} ions, and because of crystal-field splitting, two of the d orbitals have higher energies than the rest of the three. Then to allow the electron filling the upper two orbitals in Mn^{3+} to hop to Mn^{4+} , we have to make the magnetic moments of Mn^{3+} and Mn^{4+} ions the same, or otherwise after the hopping, a strong Hund energy penalty occurs.

2.4.3 Dzyaloshinskii-Moriya interaction

The **Dzyaloshinskii-Moriya interaction**

$$H = \mathbf{D} \cdot (\mathbf{S}_1 \times \mathbf{S}_2) \quad (13)$$

comes from the second order perturbation of Anderson superexchange and spin-orbital coupling (the first step being SOC and the second step being superexchange, or the inverse). The cross multiplication symbol comes when we sum $(\mathbf{S}_1 \cdot \mathbf{L}_1)(\mathbf{S}_1 \cdot \mathbf{S}_2)$ terms together. The \mathbf{D} vector appears only when the inversion symmetry is broken.

This interaction motivates spins to be *not* parallel to each other, forming vortex configurations of spins. Since the inversion symmetry is by definition broken in interfacial magnets, it can be as large as 20 % of direct exchange, and therefore is strong enough to compete with the latter. It directly gives rise to skyrmions, and from skyrmions TODO: Wei et al. Rare Metals 40, 3076 (2021).

2.4.4 The RKKY interaction

A clear demonstration of the ability for itinerant electrons to mediate the interaction between (very far) magnetic moments is such an experiment: TODO: fig 7

This oscillation of the magnetization can be attributed to the mechanism below. We know there is direct exchange interaction between a localized magnetic moment and an itinerant electron, so the spin polarization around a local magnetic moment is regulated by it. We know electrons scattered by the same impurity can interfere with each other, with a spatial interference length of $\sim 1/k_F$ – this is exactly why we see interference rings in STM around impurities. Now we see the local magnetic moment as an impurity, and if another local magnetic moment is placed in this surrounding of these spin-polarized electrons, due to its direct exchange interaction with the latter, a spatially oscillating magnetic coupling between the two local magnetic moments occurs. This is the **Ruderman–Kittel–Kasuya–Yosida (RKKY)** interaction.

3 Itinerant magnetism

3.1 Stoner magnets

Consider the density-density channel of electron-electron Coulomb repulsion $Un_\uparrow n_\downarrow$. To reduce the influence of this term in the total energy, electrons may choose to have a larger u_\uparrow and therefore a smaller n_\downarrow (or the inverse – a spontaneous symmetry breaking is involved here), and hence

$$\delta E = U(n - \delta n)(n + \delta n) + \Delta \delta n - Un^2, \quad (14)$$

where $\Delta = \delta n / \rho(E_F)$. If $\delta E < 0$, which is equivalent to

$$\rho(E_F)U > 1, \quad (15)$$

then a magnetization order is formed. Magnets with this kind of magnetization mechanism are **Stoner magnets**.

In real materials, what contributes to the Stoner mechanism are highly itinerant electrons; f orbitals, since they are highly localized, have almost no contribution to the Fermi surface and therefore don't contribute to Stoner magnetism, though they definitely contribute to localized magnetism. But this doesn't mean electrons that do contribute to the Fermi surface to have very dispersive band structures, or otherwise $\rho(E_F)$ is very low. So the Stoner criterion works best for transitional metals, and it correctly predicts that Fe and Ni are magnetic.