

Magnetism and the Periodic Table

We have seen that the paramagnetic effect, even for a single unpaired spin, is much stronger than the classical diamagnetic effect of most atoms, by roughly two orders of magnitude. And there are a significant number of atoms in the periodic table that have even stronger paramagnetic susceptibility than this owing to partially-filled inner shells. Many of these are the so-called transition metals occupying rows 4, 5, 6, and 7 of the periodic table, 10 elements in each row, as shown clearly in Fig. 1. In each of the four rows four, the 3d, 4d, 5d, or 6d shell, respectively, is partially or completely filled, and is surrounded by at least one s electron (zero orbital angular momentum) of higher principle quantum number (i.e., 4s, 5s, 6s, or 7s, respectively). The elements with partially filled d shells can have total angular momentum magnitude $|\mathbf{J}| \gg \hbar/2$ because of the effect of multiple electrons having unpaired spins. In the solid-state context, “unpaired” simply means that there is an unequal number of spins having $+\hbar/2$ (i.e., spin up) and $-\hbar/2$ (i.e., spin down). This can happen two ways, either by having an odd number of electrons in the particular d shell, or by having a majority of an even number of electron in the spin up or down orientation.

The three transition elements in row 4 just to the left of Cu are the most special paramagnetic transition elements of all. These are Fe, Co, and Ni. Their unpaired spins create a large atomic built-in moment, and the neighboring atoms interact in just the right way so that below some critical temperature, the Curie temperature, the net angular momenta on each atom spontaneously co-align in the fascinating state we know as ferromagnetism and address in the next two sections. These are also the only three elements in the periodic table whose Curie temperatures are well above 300 K.

the sequence of elements between these two that is expected to show the greatest paramagnetism.

We have stated how to calculate the net magnetic dipole moment when there is a built-in total angular momentum, and we have stated which atoms of the periodic table can create this built-in effect. But we have not explained how the built-in magnetic moment occurs in the first place except for the fact that it is correlated to unpaired spins in partially filled inner atomic shells. The detailed answer entails an explanation of the periodic table and how the electron states are filled with increasing atomic number. This requires many results from atomic physics, especially the Hartree theory of the atom, which is lengthy and beyond the scope of the book. But one aspect of this theory is critical to solid state engineering because of its impact on magnetism, which is the electron exchange interaction. In our discussion of atomic bonding in Chapter 3, we noted the covalent bond generally forms with a pair of shared electrons in a symmetric combination of spatial wavefunctions. Quantum mechanically, the pair will then have greater expectation of occupying the region between the two atoms than if they occupied antisymmetric spatial wavefunctions. This increases the shielding of the (repulsive) Coulomb between the two positively-charged nuclei and thereby reduces the total potential energy, creating a more stable bond. At the same time, the Pauli exclusion principle forces these two shared electrons to have opposite spin or, equivalently, an antisymmetric (with respect to electron exchange) overall (space-spin) wavefunction.

Although not discussed in 215A, the same type of effect occurs in ionic bonding. For example, an electron in an atom having a half-filled outermost s shell is transferred to a second atom having 5 electrons occupying an outermost p shell (6 being the maximum occupancy). The outer shells of both electrons start with a built-in total angular momentum, but each vanishes once the electron transfer occurs. When combined with the covalent bonding effect, it leads to a rough rule that the outermost-shell (i.e., “valence”) electrons of solids rarely, if ever, contribute to paramagnetism in solids because they are too involved in the bonding process, which tends to cancel the total angular momentum of the resulting solid.

Quite another effect occurs between two electrons in free space or in the shielded environment of an inner d or f shell. In this case the Coulomb repulsion between the

electrons can be the most important interaction and always contributes a positive potential energy [$q_1 q_2 / (4\pi\epsilon_0 r)$, where r is the interelectron separation] since the charges are the same sign. Hence, a combination of electronic wavefunctions that maximizes their separation will minimize the pair potential and, therefore, be energetically favored. Similar to the case for interatomic bonding, the greatest separation is created the antisymmetric combination of spatial wave functions. And by Pauli exclusion, this means that the spin wave functions will be symmetric (i.e., both spin up, or both spin down). So the sequence of transition metals and rare-earth elements in the periodic table can (and do) fill their d or f shells with increasing numbers of co-aligned spins and, therefore, non zero net spin angular momentum in the respective shell.

Non-zero net spin angular momentum, S , is important for two reasons. First, it usually creates non-zero net total angular momentum and, thus a built-in magnetic dipole moment. But non-zero net orbital angular momentum can and often does the same thing, depending on the particular atom. So the second important effect is the surprisingly strong interaction between neighboring atoms of non-zero S . This is strictly a quantum mechanical effect, unexplained by classical physics, and essential to the phenomenon of ferromagnetism as we shall see in the following sections.