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Cross-relaxation Effects in Magnetic Resonance

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A review is given of the energy transfer between different parts of a system of spins, isolated from the lattice. If the parts are separated in space, such energy transfer takes place by spin-diffusion. The attention in this review will be focused on the transfer of energy, without a spatial gradient, between two different species of spins, the conversion of Zeeman energy into exchange energy or dipolar energy, etc. The discussion will be quite general in nature and will be equally valid for electronic and nuclear spin systems. It is concerned with the question how a single uniform spin temperature introduced in the thermodynamic model of Casimir and du Pré is established in a spin system which is isolated from the lattice. This question does not arise in the case of isolated spins. A very dilute paramagnetic material or an irradiated crystal containing a few free redicals are examples of a situation, in which thermal equilibrium can only be established through interaction with the lattice.

Consider, however, an assembly of spins S in a magnetic field H_0, so that the Zeeman energy $\mathcal{H}_Z$ is large compared to the interaction energy. The latter is divided into two parts. The first part consists of the exchange energy and that portion of the dipolar energy which commutes with the Zeeman energy. It will be denoted shortly by $\mathcal{H}_{ex}$. The second part contains the offdiagonal elements of the dipolar energy. A Boltzmann distribution among the $2S + 1$ Zeeman levels will rapidly be established in a time of the order of T_2. It will take however very much longer for the thermal equilibrium to be established between $\mathcal{H}_Z$ and $\mathcal{H}_{ex}$, when $\mathcal{H}_Z \gg \mathcal{H}_{ex}$. It is then necessary to consider how $\mathcal{H}_{ex}$ can take up large quanta $h\nu_0$, as was first done by Kronig and Bouwkamp [2]. The characteristic time T_{21} for this cross-relation process is roughly given by

$$T_{21} \sim T_2 \exp(+H_0^2/\Delta H^2)$$

Crudely it can be said that the transition probability T_{21}^{-1} is determined by the wing of the ordinary magnetic resonance near zero frequency. A

much more precise description can be found in references [3 and 4]. This same process gives rise to a relaxation at intermediate frequencies around $\omega \sim T_{21}^{-1}$ in the non-resonant experiments carried out by Gorter and coworkers[5].

Next consider two spins with different gyromagnetic ratios. The classical example is the Li^7 and F^{19} system in LiF. If the Li^7 resonance is saturated in a large external field, nothing happens to the F^{19} system which is completely isolated from the Li^7 system. In zero field complete thermodynamic equilibrium is established between all spins, in a time of the order of $T_2 \sim 10^{-4}$ sec. After the early experiments of Pound, Purcell [6] and Ramsey this was shown conclusively by Abragam and Proctor [7]. Pershan has investigated in detail the rate at which equilibrium is established in intermediate fields. He finds that cross-relaxation takes place by a process in which two Li^7 spins and one F^{19} spin flip simultaneously. This process conserves more nearly the Zeeman energy and the smaller balance can be taken up more easily by the dipolar interaction of the spin array. The data can be represented rather well by the relation,

$$T_{21} \approx T_2 \frac{\Delta\nu^2}{(2\nu_{Li} - \nu_F)^2} \exp\left[(2\nu_{Li} - \nu_F)^2/2\ (2\Delta\nu_{Li}^2 + \Delta\nu_F^2)\right]$$

Since the second moments of the Li^7 and F^{19} resonance have some anisotropy and occur in the exponent of the gaussian function, T_{21} is highly anisotropic. A more precise mathematical formulation of the cross-relaxation problem can be found in reference [4]), but crudely it can be said to be due to the overlap of the satellite Li^7 resonance at $2\nu_{Li}$ and the F^{19} resonance at ν_Z.

A similar state of affairs exists in paramagnetic salts with different magnetic ions, or with one kind of ion with different crystalline field splittings and/or hyperfine splittings. Higher order processes in which several spins flip simultaneously can still be faster than spin-lattice relaxation, if the sum of the energies involved in the simultaneous transitions is zero or of the order of magnitude of the dipolar interaction. Numerous experimental data have recently appeared[8] on such cross-relaxation situations, stimulated largely by the development of solid state masers. Several examples of both beneficial and detrimental effects to maser action are given.

a) In a concentrated magnetic material the dipolar interaction is so large and cross-relaxation so fast between all spin levels, that the whole

spin system is in thermal equilibrium. In this case power fed in at the pump frequency will heat up the spin system uniformly and completely. No maser action is possible.

b) In diluted magnetic materials the various spin resonances are sufficiently isolated. The higher the temperature the larger is the maximum permissible concentration of magnetic ions to obtain maser action. The relative magnitude of cross-relaxation and spin-lattice relaxation times is the determining factor. The low-frequency limit of a maser is determined by the overlap of resonance lines.

c) Pump power at a sharply defined frequency produces nevertheless a homogeneous saturation of the spin resonance, even if this resonance is broadened by inhomogeneous local fields. This is not true if the inhomogeneity has a large-scale macroscopic nature. If the width is caused by nuclear magnetic moments, cross-relaxation processes involving nuclear spin flips as well should also be considered.

The stimulated emission at the maser frequency occurs likewise over the entire width of a homogeneously inverted resonance line. This result is very important for gain-bandwidth considerations.

d) Cross-relaxation can enhance the relaxation rate or saturation level of individual transitions among the spin levels. It can therefore either enhance or reduce the gain-bandwidth product at the maser transition.

e) Higher-order cross-relaxation process permit maser action at a higher frequency than the pump frequency. Such multiple spin transitions have sometimes been denoted by harmonic cross coupling. Cross-relaxation up to the 11th harmonic has been observed in ruby. Such a process involves the cooperation of twelve spins. It is of course highly concentration dependent. At still higher concentrations everything merges into one single system with a common temperature and a single spin-lattice relaxation time.

Cross-relaxation experiments show how fast and to what extent different parts of a system of spins come into mutual equilibrium. They are a laboratory for statistical mechanics and elucidate the concept of spin temperature [9].

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