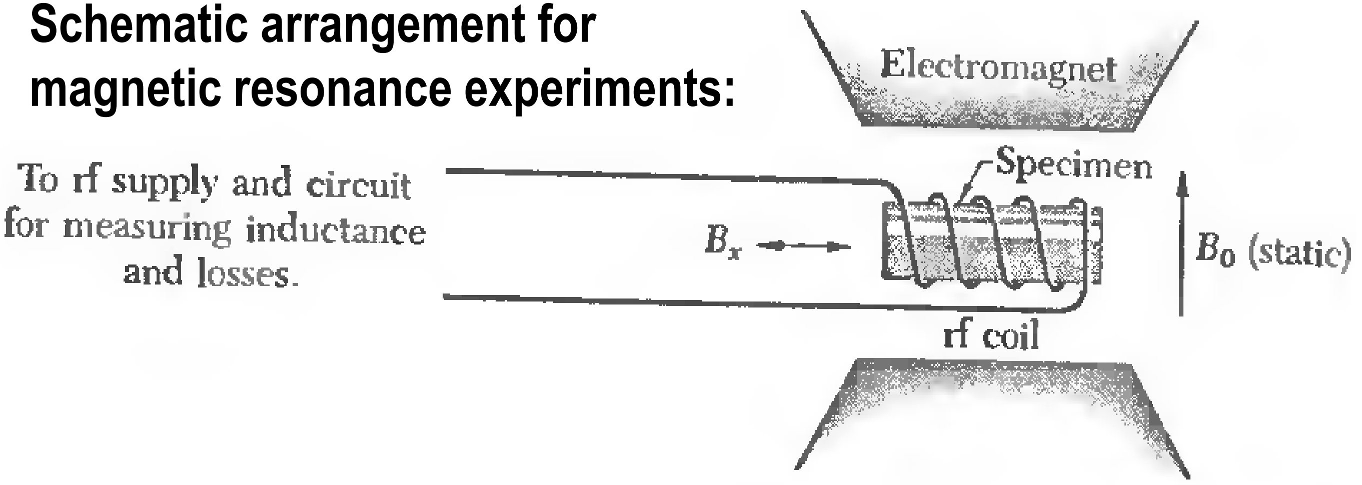
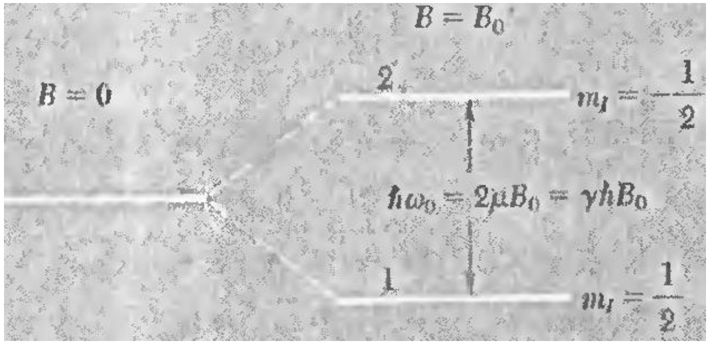
Magnetic resonance (2)

Schematic arrangement for magnetic resonance experiments:





Energy level splitting of a nucleus of spin 1/2 in a static magnetic field B_0.

Magnetic moment of a nucleus $\boldsymbol{\mu} = \gamma\hbar\mathbf{I}$

The energy of interaction with the applied magnetic field is $U = -\boldsymbol{\mu}\cdot\mathbf{B}_a$

For I=1/2 the magnetic resonance frequency

$$\omega_0 = \gamma B_0$$

where the constant γ depends on the magnetic moment

For proton

$$\gamma = 2.675 \times 10^4\ \mathrm{s}^{-1}\ \mathrm{gauss}^{-1} = 2.675 \times 10^8\ \mathrm{s}^{-1}\ \mathrm{tesla}^{-1}$$

Table 1 Nuclear magnetic resonance data

For every element the most abundant magnetic isotope is shown. After Varian Associates NMR Table.

Most abundant isotope with nonzero nuclear spin
Nuclear spin; in units of $\hbar$
Natural abundance of isotope, in percent
Nuclear magnetic moment, in units of $e\hbar/2M_pc$

H^{1}																	He^{3}
1/2																	1/2
99.98																	10^{-6}
2.792																	−2.127
Li^{7}	Be^{9}											B^{11}	C^{13}	N^{14}	O^{17}	F^{19}	Ne^{21}
3/2	3/2											3/2	1/2	1	5/2	1/2	3/2
92.57	100.											81.17	1.108	99.64	0.04	100.	0.257
3.256	−1.177											2.688	0.702	0.404	−1.893	2.627	−0.662
Na^{23}	Mg^{25}											Al^{27}	Si^{29}	P^{31}	S^{33}	Cl^{35}	Ar
3/2	5/2											5/2	1/2	1/2	3/2	3/2	
100.	10.05											100.	4.70	100.	0.74	75.4	
2.216	0.855											3.639	0.555	1.131	0.643	0.821	
K^{39}	Ca^{43}	Sc^{45}	Ti^{47}	V^{51}	Cr^{53}	Mn^{55}	Fe^{57}	Co^{59}	Ni^{61}	Cu^{63}	Zn^{67}	Ga^{69}	Ge^{73}	As^{75}	Se^{77}	Br^{79}	Kr^{83}
3/2	7/2	7/2	5/2	7/2	3/2	5/2	1/2	7/2	3/2	3/2	5/2	3/2	9/2	3/2	1/2	3/2	9/2
93.08	0.13	100.	7.75	~100.	9.54	100.	2.245	100.	1.25	69.09	4.12	60.2	7.61	100.	7.50	50.57	11.55
0.391	−1.315	4.749	0.787	5.139	0.474	3.461	0.090	4.639	0.746	2.221	0.874	2.011	0.877	1.435	0.533	2.099	−0.967
Rb^{85}	Sr^{87}	Y^{89}	Zr^{91}	Nb^{93}	Mo^{95}	Tc	Ru^{101}	Rh^{103}	Pd^{105}	Ag^{107}	Cd^{111}	In^{115}	Sn^{119}	Sb^{121}	Te^{125}	I^{127}	Xe^{129}
5/2	9/2	1/2	5/2	9/2	5/2		5/2	1/2	5/2	1/2	1/2	9/2	1/2	5/2	1/2	5/2	1/2
72.8	7.02	100.	11.23	100.	15.78		16.98	100.	22.23	51.35	12.86	95.84	8.68	57.25	7.03	100.	26.24
1.348	1.089	0.137	1.298	6.144	0.910		−0.69	0.088	−0.57	−0.113	−0.592	5.507	−1.041	3.342	−0.882	2.794	−0.773
Cs^{133}	Ba^{137}	La^{139}	Hf^{177}	Ta^{181}	W^{183}	Re^{187}	Os^{189}	Ir^{193}	Pt^{195}	Au^{197}	Hg^{199}	Tl^{205}	Pb^{207}	Bi^{209}	Po	At	Rn
7/2	3/2	7/2	7/2	7/2	1/2	5/2	3/2	3/2	1/2	3/2	1/2	1/2	1/2	9/2			
100.	11.32	99.9	18.39	100.	14.28	62.93	16.1	61.5	33.7	100.	16.86	70.48	21.11	100.			
2.564	0.931	2.761	0.61	2.340	0.115	3.176	0.651	0.17	0.600	0.144	0.498	1.612	0.584	4.039			
Fr	Ra	Ac															

Ce^{141}*	Pr^{141}	Nd^{143}	Pm	Sm^{147}	Eu^{153}	Gd^{157}	Tb^{159}	Dy^{163}	Ho^{165}	Er^{167}	Tm^{169}	Yb^{173}	Lu^{175}
7/2	5/2	7/2		7/2	5/2	3/2	3/2	5/2	7/2	7/2	1/2	5/2	7/2
—	100.	12.20		15.07	52.23	15.64	100.	24.97	100.	22.82	100.	16.08	97.40
0.16	3.92	−1.25		−0.68	1.521	−0.34	1.52	−0.53	3.31	0.48	−0.20	−0.677	2.9
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Equations of motion for magnetic moment

The time evolution of a spin vector $\mathbf{I}$ is given by $\hbar d\mathbf{I}/dt = \boldsymbol{\mu} \times \mathbf{B}_a$

or for its magnetic moment $d\boldsymbol{\mu}/dt = \gamma\boldsymbol{\mu} \times \mathbf{B}_a$

The evolution of a total magnetization in external field $d\mathbf{M}/dt = \gamma\mathbf{M} \times \mathbf{B}_a$

In thermal equilibrium the population of two energy levels is given by the ratio: $(N_2/N_1)_0 = \exp(-2\mu B_0/k_BT)$

and the total magnetization is given by $M_0 = N\mu \tanh(\mu B/k_BT)$

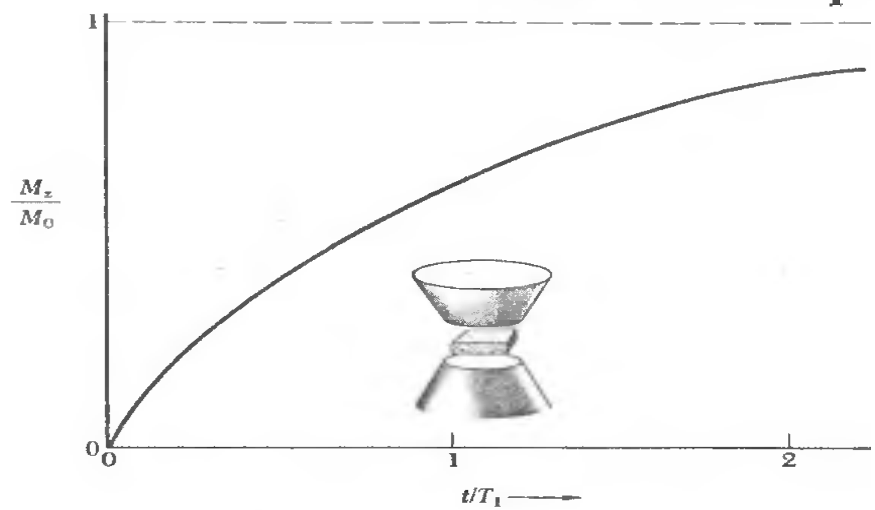
When magnetization is not in equilibrium, it approaches equilibrium at a rate proportional to the departure from the equilibrium value M_0:

$$\frac{dM_z}{dt} = \frac{M_0 - M_z}{T_1}$$

This linear differential equation can be solved easily and gives

$$M_z(t) = M_0[1 - \exp(-t/T_1)]$$

T_1 is called the longitudinal relaxation time or the spin-lattice relaxation time.



Longitudinal magnetization relaxation

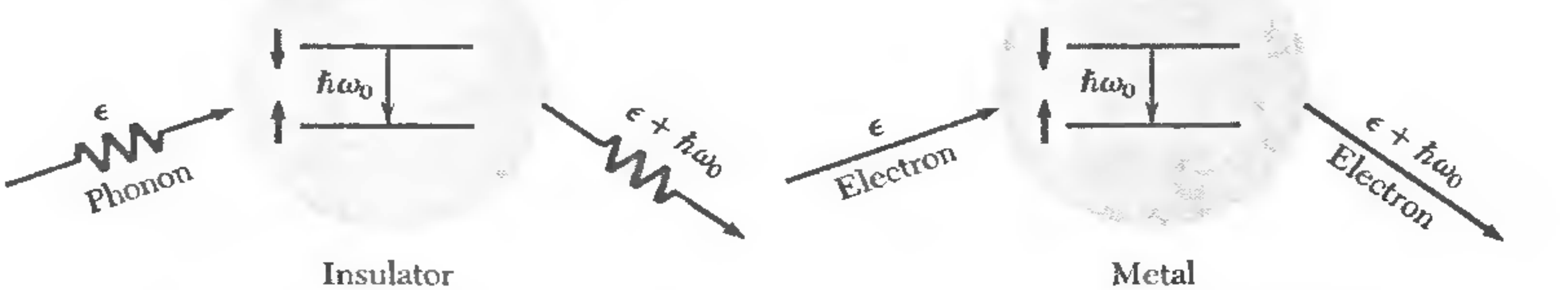


Figure 4a Some important processes that contribute to longitudinal magnetization relaxation in an insulator and in a metal. For the insulator we show a phonon scattered inelastically by the spin system. The spin system moves to a lower energy state, and the emitted phonon has higher energy by $\hbar\omega_0$ than the absorbed phonon. For the metal we show a similar inelastic scattering process in which a conduction electron is scattered.

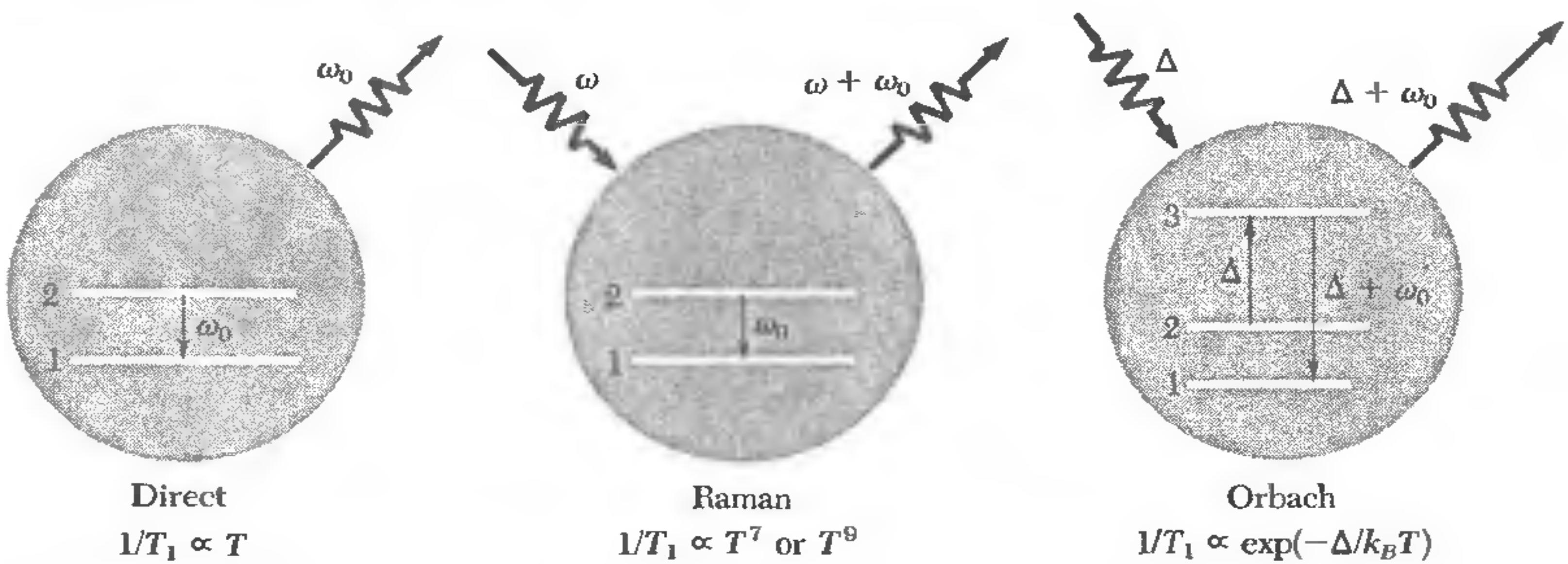


Figure 4b Spin relaxation from $2 \rightarrow 1$ by phonon emission, phonon scattering, and a two-stage phonon process. The temperature dependence of the longitudinal relaxation time T_1 is shown for the several processes.

Longitudinal magnetization relaxation (experiment)

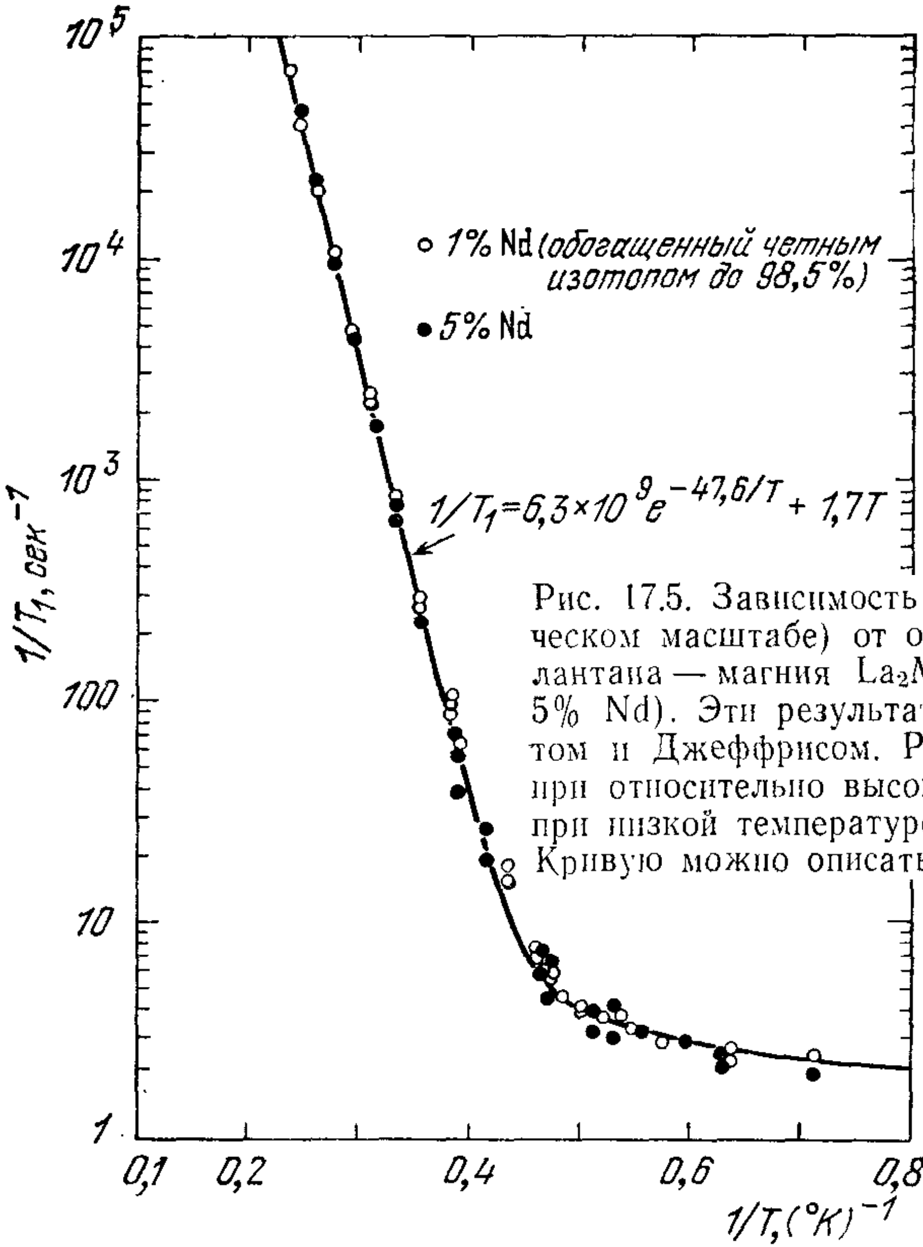


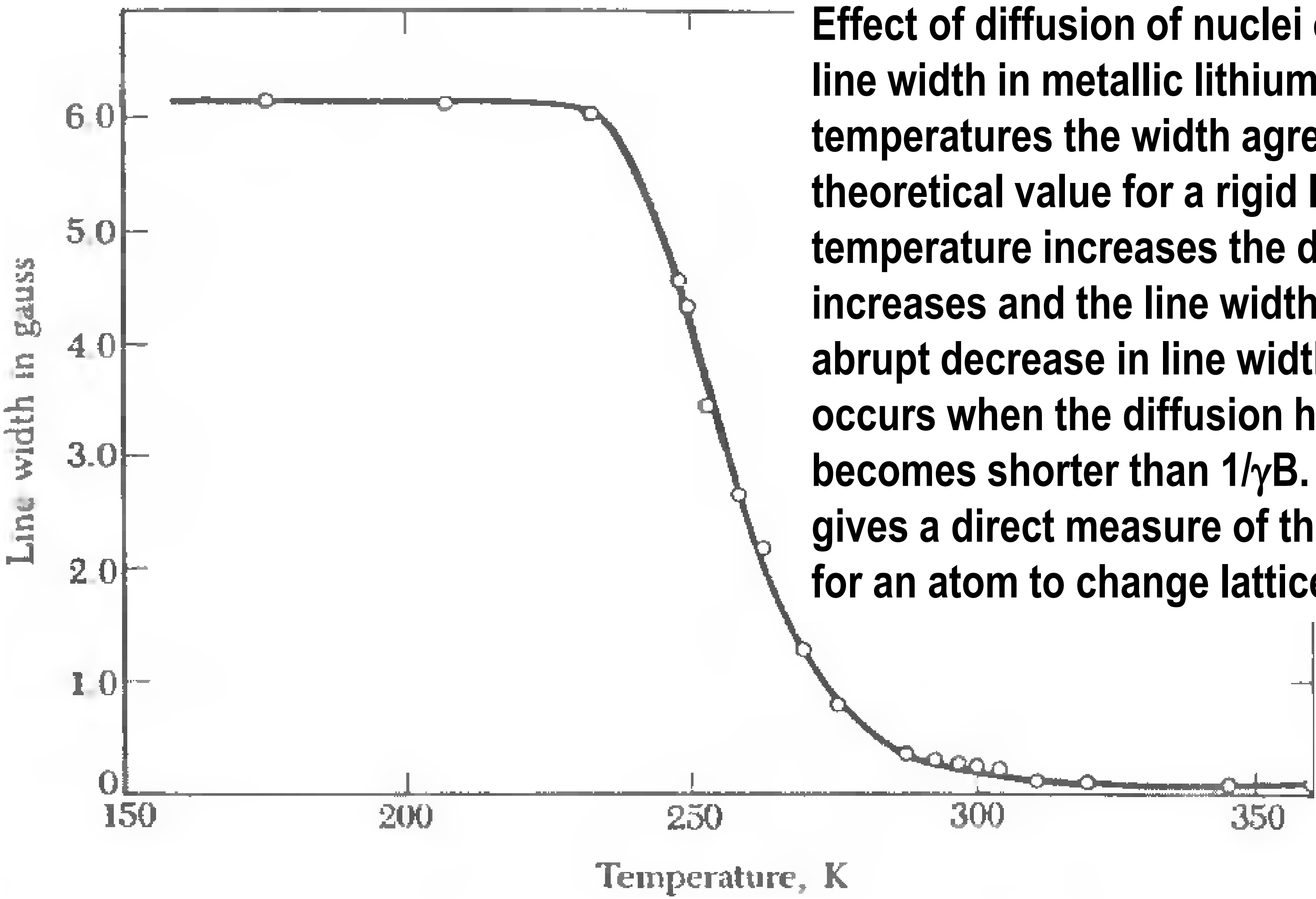
Рис. 17.5. Зависимость быстроты продольной релаксации $1/T_1$ (в логарифмическом масштабе) от обратной температуры для кристалла двойного нитрата лантана — магния $La_2Mg_3(NO_3)_{12}\cdot 24H_2O$ с примесью неодима (1% Nd и 5% Nd). Эти результаты получены в интервале температур 1,4—4,3 °K Скоттом и Джеффрисом. Результаты убедительно указывают на процесс Орбаха при относительно высоких температурах и на прямой однофононный процесс при низкой температуре. Частота $\nu = 9,37$ ГГц, магнитное поле $B = 2,48$ кГс. Кривую можно описать аналитически: $1/T_1 = 6,3\cdot 10^9\, e^{-47,6/T} + 1,7\, T$.

Motional Narrowing of NMR line

The effective magnetic field due to magnetic dipole-dipole interaction is

$$\Delta B = \frac{3(\boldsymbol{\mu}_2 \cdot \mathbf{r}_{12})\mathbf{r}_{12} - \boldsymbol{\mu}_2 r_{12}^2}{r_{12}^5}$$

It effectively averages to almost zero when the atoms move fast enough.



Effect of diffusion of nuclei on the Li^7 NMR line width in metallic lithium. At low temperatures the width agrees with the theoretical value for a rigid lattice. As the temperature increases the diffusion rate increases and the line width decreases. The abrupt decrease in line width above T = 230 K occurs when the diffusion hopping time becomes shorter than $1/\gamma B$. The experiment gives a direct measure of the hopping time for an atom to change lattice sites.

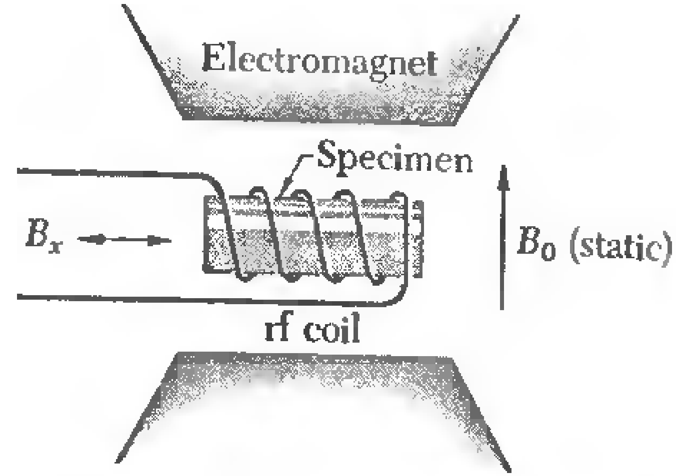
The Bloch equations
for magnetic moment evolution with time

$$dM_x/dt = \gamma(\mathbf{M}\times\mathbf{B})_x - M_x/T_2\ ;$$

$$dM_y/dt = \gamma(\mathbf{M}\times\mathbf{B})_y - M_y/T_2\ ;$$

$$dM_z/dt = \gamma(\mathbf{M}\times\mathbf{B})_z + (M_0 - M_z)/T_1$$

T_2 is called the transverse relaxation time

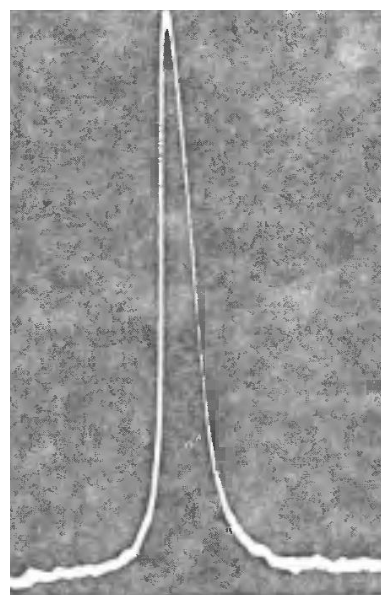


The transverse spin relaxation does not need energy change, => often $T_2 \ll T_1$

Solving the Bloch equations we find the resonance power absorption in NMR experiments with resonance frequency ω_0 determined by Zeeman energy splitting in B_0:

$$\mathcal{P}(\omega) = \frac{\omega\gamma M_z T_2}{1 + (\omega_0 - \omega)^2 T_2^2} B_1^2$$

The resonance half-width $(\Delta\omega)_{1/2} = 1/T_2$



Proton resonance absorption in water.