Low-Frequency Detected EPR: Principles and Applications

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Abstract. The experimental works described are performed by the authors over last two decades by means of the LFD EPR technique. The essence of this method is low-frequency detection of the longitudinal spin magnetization while the magnetic resonance is excited by a strong microwave field. The first kind of LFD EPR is the enhanced longitudinal susceptibility effect (ELSE) which has been elaborated and applied to study spin thermodynamics in solids since 1972. Various applications of ELSE are described such as direct measuring of the spin-spin interaction temperature $T_{ss}$ in the course of resonance saturation, spin-lattice and cross relaxation, dynamic nuclear polarization etc. Another version of LFD EPR was employed to study electron spin-lattice relaxation of paramagnetic centers in high-temperature superconductors (HTSC). Recent experimental data are presented on the electron spin-lattice relaxation of Cu$^{2+}$ ions in YBa$_2$Cu$_3$O$_{6+x}$ at various temperatures and $x$ values.

1. Introduction

All methods of registering the magnetic resonance signals can be divided into two groups: direct and indirect ones. In the first case one observes the resonance response of the sample at its intrinsic (Larmor) frequency $\omega_0 = \gamma H_0$, where $H_0$ is an external magnetic field. This category includes the most popular steady-state and pulse methods allowing one to record the resonance spectra, free induction decay, spin echo and so on. Unlike this, the indirect methods deal with the changes produced in a sample under the action of the resonant pumping. The indirect methods are very diversified, from the classic atomic beam technique by Rabi up to modern optically detected magnetic resonance (ODMR), electron-nuclear double resonance (ENDOR), etc.

Note that in two latter cases the detection is performed at a frequency which is much higher than that used for the resonant pumping. This is a great advantage of the ODMR and ENDOR techniques because of their benefit in sensitivity.
This paper is concerned with the opposite situation when the detection of the magnetic resonance is carried out at a relatively low frequency $\Omega \ll \omega_0$, whereas a sufficiently strong microwave field $H_1 \cdot \exp(i\omega t)$, $\omega \approx \omega_0$ is applied only to saturate the spin system (or to act upon this system by a more complicated way).

At a first glance such a technique seems ineffective because of lack of sensitivity. However in some cases the inequality $\Omega \ll \omega_0$ can be compensated by a giant rise of the detected signal. As an example one can consider the dynamic nuclear polarization (DNP); in this case the low-frequency NMR signal is increased by several orders of magnitude upon the action of the microwave saturation of the EPR line. On the other hand, the low-frequency detection can be sometimes surprisingly useful, allowing one to get information which is difficult or even impossible to obtain by traditional means.

In this paper we present the results of our works performed by means of various kinds of the low-frequency detected EPR (LFD EPR). In Section 2, the "encheded longitudinal susceptibility effect" (ELSE) is described. This technique suggested first in 1973 was then applied to study the evolution of spin temperatures in paramagnetic solids. Finally, Section 3 is concerned with our recent experimental work where the low-frequency detection of the longitudinal spin magnetization enabled us to investigate electron spin-lattice relaxation of paramagnetic centers in high-temperature superconductors (HTSC).

2. The Enhanced Longitudinal Susceptibility Effect (ELSE)

2.1. Physical Grounds

Consider a paramagnetic solid containing spins $S$ (electronic or nuclear) placed in a static external magnetic field $H_0$ where the Larmor frequency of the spins is $\omega_0 = \gamma H_0$. Let $H_0$ be much larger than the local field $H_L = \omega_L/\gamma$ caused by spin-spin interactions (as a rule, these are magnetic dipole-dipole interactions, but in general their origin may be different: exchange, hyperfine, etc). Then the main term in the Hamiltonian of the spin system is that determined by Zeeman interaction $H_\text{Z}$ of the spins with the field $H_0$. The spin-spin interactions being usually much stronger in solids than the spin-lattice relaxation, provides the establishment of the internal quasi-equilibrium in two approximately separate energy subsystems: the Zeeman reservoir (ZR) and the spin-spin interaction reservoir (SSR), the latter being constituted by the secular part $\mathcal{H}_\text{SS}^0$ of the spin-spin interaction Hamiltonian.

This two-temperature concept was introduced into the theory of magnetic resonance by Provotorov [4] as a natural development of the spin thermodynamics created by Casimir and Du Pré [5], Gorter [6], Abragam and others [1, 7]. The most important physical consequence of the Provotorov equations is a strong cooling of SSR as a result of saturation of magnetic resonance with a frequency offset $\Lambda = \omega - \omega_0$. Under a strong saturation one gets for the cooling factor $E [8, 9]$: 