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Trends

Sensitive detection of NMR for thin films

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ABSTRACT

NMR can provide valuable information about thin films, but its relatively low sensitivity allows data acquisition only from bulk samples. The sensitivity problem is circumvented by detection schemes with higher sensitivity and/or enhanced polarization. In most of these ingenious techniques, electrons play a central role through hyperfine interactions with the nuclei of interest or the conversion of the spin orientation to an electric charge. The state of the art in NMR is the control of a single nuclear spin state, the complete form of which is one of the ultimate goals of nanotechnology.

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1. Introduction

Nuclear magnetic resonance is a powerful research tool that has been widely harnessed as a characterization and imaging technique in physics, chemistry, biology, and other engineering fields. It may not be an accident that X-ray CT and MRI, which are the two fundamental diagnosis tools most frequently used in hospitals, are based on X-rays and NMR, respectively. The local properties of electronic and nuclear states generally affect NMR signals and are reflected in the spectrum. The interactions between nuclei and electrons are analyzed to obtain the states and

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dynamics of electrons in physics, whereas interactions among nuclei are often evaluated to determine molecular structures in chemistry and biology. Because a nuclear spin interacting very weakly with electrons is adopted as a probe in NMR, measurements scarcely disturb the physical states of samples because these states are mostly determined by the electrons. This noninvasive probing capability is well utilized in imaging. NMR is also the tool used to demonstrate quantum computing for the first time. It is difficult to imagine that the quantum control of a single quantum state such as a spin, which is one of the ultimate goals of nanotechnology, can be accomplished without magnetic resonance. The ability to observe the static and dynamic interactions of a selected nucleus is still generating new applications in various fields.

The advancement of nanotechnology has revealed unprecedented phenomena and has led to the development of new quantum devices. Thin films and nano-sized samples have quite different properties from their bulk forms owing to the effects of reduced dimensions, interfaces, and quantum sizes. NMR can provide valuable information about these effects, but unfortunately, conventional NMR employing an inductive detection scheme can scarcely obtain signals from thin film or nano-sized samples owing to its relatively low sensitivity. A gyromagnetic ratio of electrons three orders of magnitude larger than that of the nuclei results in higher sensitivity to ESR by six orders of magnitude compared to NMR given the same magnetic field and temperature. Usually, 10^{10}–10^{12} electron spins are necessary for ESR experiments whereas 10^{16}–10^{18} nuclear spins are necessary for NMR in the range from liquid helium to room temperature. Thin-film samples with submicron thicknesses have only 0.01% of the nuclear spins of bulk samples with a thickness of a few millimeters. A condensed-matter sample with a volume of 1 cm^3 contains approximately 10^{22} atoms. Therefore, the lower limit of the thickness of a thin-film sample with an area of 1 cm^2 for an NMR experiment is 10 nm at the temperature of liquid helium with regard to the number of spins. In practice, it is nontrivial to determine the NMR signal from films even 1 μm thick owing to the low filling factor of a probe coil. An ESR study of thin films is more common.

Because the important point is the low sensitivity, the question resolves itself largely as a signal-to-noise ratio (SNR) issue. The first task undertaken by NMR researchers in a laboratory when pursuing a higher SNR may be to decrease the temperature and/or increase the magnetic field to enhance the nuclear polarization and reduce thermal noise. Improving the electronics of a spectrometer will surely help when seeking a better SNR. Samples are prepared in special ways to provide a sufficient number of spins. Multilayer-structured samples may contain enough spins for an NMR study of thin films consisting of a few atomic layers. Powder samples are frequently used to increase the surface area when the surface properties are investigated. Averaging is always an option to use at the last moment of data acquisition after all of these efforts have been made.

In addition to these common practices, several ingenious techniques have been developed to increase the sensitivity of NMR by several orders of magnitude such that thin films can be observed. Hyperfine interaction is sometimes a curse to magnetic resonance researchers because it generates unwanted broadening in the ESR and NMR spectra. At the same time, it is also a blessing in terms of how it makes these techniques available. These techniques can be largely categorized into those that rely on sensitive detection and those that rely on polarization enhancement. Detection schemes more sensitive than induction include optical, electric, and mechanical methods, which are optically detected magnetic resonance (ODMR [1]), electrically detected magnetic resonance (EDMR [2]) and magnetic resonance force microscopy (MRFM [3]), respectively. With these methods, electron nuclear double resonance (ENDOR [4]) and $\beta-$NMR [5], can be said to belong to the first category, with the hyperpolarization and enhancement effect [6], in magnets belonging to the second. In this review, the working principles of these special techniques and recent applications to thin films are introduced. Techniques with relatively short histories or that are not as familiar as others are discussed in more detail. All studies cited below were obtained from research on (or are applicable to) NMR for thin films.

2. ENDOR

The first apparent option for magnetic resonance researchers when seeking to obtain the NMR signals of thin films would be to check whether ENDOR is applicable. ENDOR is an indirect means of measuring NMR via ESR exploiting hyperfine interaction. Therefore, one requirement is that the sample should be paramagnetic, and the hyperfine interaction between the spins of the nuclei of interest and electrons should be larger than the linewidth of the ESR spectrum. Most of the physical quantities of NMR, such as the spectral shape and the nuclear relaxation times, can be determined by ENDOR. Phosphorous-doped silicon is one of the typical systems feasible for study using ENDOR. A phosphorous donor electron is bound to a spin-1/2 nucleus of the same atom. The separation of two peaks in the ESR spectrum due to hyperfine interaction is 42 G, which is one order of magnitude greater than the linewidth of the peaks.

The spin Hamiltonian of a system consisting of a nucleus coupled with an electron in a magnetic field is

$$H = g_e\mu_B BS_z - g_n\mu_n BI_z + a\vec{S}\cdot\vec{I},$$

where S and I are the electron and nuclear spins, respectively; a is the hyperfine interaction constant; and g_e and g_n are the gyromagnetic ratios of the electron and nuclear spins, respectively. The system has four split energy levels in the magnetic field if the spin of the nucleus is ½—for example, as depicted in Fig. 1(a). When the Zeeman energy of a nucleus is much larger than the hyperfine interaction, the states corresponding to these energy levels are the $|\uparrow\uparrow>$, $|\uparrow\downarrow>$, $|\downarrow\uparrow>$, and $|\downarrow\downarrow>$ states, where the first and second arrows represent the spins of the electron and nucleus,

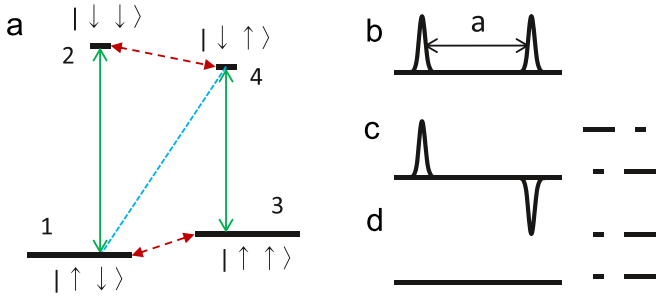

Fig. 1. (a) The energy levels and transitions in a system consisting of a spin-1/2 nucleus and an electron under a strong magnetic field. The first and second arrows represent the spins of the electron and nucleus, respectively. The transition between states 1 and 2 or 3 and 4 (green solid lines) corresponds to ESR, and the transition between the states 1 and 3 or 2 and 4 (red dashed lines) corresponds to NMR. The blue dotted line represents the cross-relaxation of the nuclear and electric flip–flop. The lengths of the bars representing the energy levels are drawn such that they are proportional to the population in thermal equilibrium. In the scale of this figure, the population difference between the up and down nuclear spin states is barely noticeable. (b) ESR peaks separated by hyperfine interaction. (c) ESR spectrum after the inversion of states 1 and 2 (d) ESR spectrum after the inversion of states 1 and 2 followed by the inversion of states 2 and 4. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)