Nuclear Magnetic Resonance Laboratory course
Assignment 4

NMR on metals I: Aluminium metal

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Abstract

Nuclear Magnetic Resonance (NMR) spectroscopy has become a cornerstone technique in modern chemistry and biology. It is primarily used to study the structure, dynamics, and interactions of molecules. In biology, NMR is invaluable for determining the three-dimensional structures of proteins, nucleic acids, and other complex biomolecules in solution. This helps researchers understand how these molecules function in the body, how they interact with other molecules, and how they change under different conditions. In chemistry, NMR is widely used to identify unknown compounds, analyze the purity of samples, and study chemical reactions. Its applications range from drug discovery to studying metabolic processes and beyond.

The origins of NMR lie, however, in physics, particularly in the study of atomic nuclei within metallic systems. The earliest NMR experiments, conducted in the 1940s, were groundbreaking in that they revealed how atomic nuclei in a magnetic field could absorb and re-emit radiofrequency radiation. These experiments were crucial in understanding the magnetic properties of metals and alloys. Physicists used NMR to explore the quantum mechanical properties of nuclei, which opened the door to a deeper understanding of solid-state physics and the magnetic behavior of materials. This foundational work laid the groundwork for the development of NMR as a powerful tool across various scientific disciplines.

In this experiment, you'll learn how to detect and analyze NMR signals specifically in metallic systems, an application that harkens back to the origins of NMR. Metals have unique electronic environments that affect the behavior of atomic nuclei, leading to distinctive NMR signals. The experiment will guide you through the process of setting up the NMR equipment, calibrating it for metallic samples, and interpreting the resulting data. You'll also learn to differentiate these signals from those generated by non-metallic compounds, which is important because the NMR response of metals is often more complex due to factors like conduction electrons and magnetic susceptibility. Understanding these differences is crucial for correctly interpreting NMR data in materials science and solid-state physics.

1 Theoretical background

For these experiments, you will need the following theoretical background. Please prepare necessary mathematical expressions and derivations:

- Discuss the underlying mechanism responsible for the Knight shift observed in metallic systems.
- Elaborate on the influence of electron-nuclear hyperfine interactions on nuclear relaxation times in metals.
- Define the Korringa relation and explain the physical insights that can be derived from it.
- Provide an overview of the crystallographic structure of metallic aluminum, emphasizing its relevance to NMR studies.
- Describe how homonuclear dipole-dipole interactions can be utilized to estimate interatomic distances in a solid-state system.

- Outline the experimental methods for determining frequency shifts, such as chemical shifts or Knight shifts, with specific reference to a) a standard material containing identical nuclei and b) the resonance frequency of metallic copper, considering the known Knight shift for ^{63,65}Cu.

2 Tasks

Please work on the tasks step-by-step and summarize your observations thoroughly and logically when you hand in the assignment. Please provide data plots and calculations to underline your conclusions. We recommend the use of ONMR running in Origin7 or later, for data analysis.

1. Utilize a pre-prepared coil containing metallic aluminum as the sample.
2. Calibrate and adjust the coil to the resonance frequency corresponding to the ^{27}Al nucleus at the specific magnetic field strength.
3. Optimize the digitization parameters to ensure accurate signal acquisition.
4. Fine-tune the pulse lengths to achieve optimal excitation of the ^{27}Al nuclei.
5. Measure the spin-lattice relaxation times (T1) for the ^{27}Al nuclei. a high-resolution ^{27}Al NMR spectrum, employing longer dwell times for enhanced spectral detail.
6. Re-tune and match the coil to the resonance frequencies of ^{63}Cu or ^{65}Cu, and record a well-resolved NMR spectrum for copper.
7. Plot the ^{27}Al NMR spectrum using the Knight shift scale, as determined from the resonance frequency of the metallic copper coil.
8. Estimate the average interatomic distance between Al atoms in face-centered cubic (fcc) aluminum using the dipolar coupling constant.
9. Plot the spin-lattice relaxation time (T1) data and perform a fit to the experimental data.
10. Evaluate whether the Korringa ratio is consistent with the theoretical constant $\left(\frac{\gamma_e}{\gamma_n}\right)^2 \cdot \frac{\hbar}{4\pi k_B}$. Discuss potential reasons for any observed discrepancies.

3 Literature

- Eiichi Fukushima, *Experimental pulse NMR - a nuts and bolts approach*
- Dustin Wheeler and Mark Conradi, *Practical Exercises for Learning to Construct NMR/MRI Probe Circuits*
- Carter, Bennett and Kahan, *Metallic shifts in NMR*
- Meier, T. (2016). High Sensitivity Nuclear Magnetic Resonance at Extreme Pressures [Leipzig University], $http://www.qucosa.de/recherche/frontdoor/?tx_slubopus4frontend[id] = 20390$