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Development of the ^{8}Li cross-relaxation technique: Applications in semiconductors and other condensed matter systems

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Abstract

The so-called "cross-relaxation" method is a powerful technique that can be used to provide detailed structural and site information on impurities in condensed matter systems, including semiconductors. In this paper, we report on the progress of its development at the new ^{8}Li β-detected nuclear magnetic resonance (β-NMR) facility located in TRIUMF in Vancouver, Canada. We present first measurements using this method on a Cu single crystal and discuss future application for studies of isolated impurities in semiconductors.

Keywords: Lithium; Cross relaxation; Site; Structure; β-Detected NMR

1. Introduction

Impurities, defects and disorder play an important role in the behavior of many solids [1–7]. In semiconductors, impurities can dramatically change the electronic and optical properties of their host. In situations where it is difficult to directly study the *isolated* impurity, it is still possible to obtain considerable information on these centers if one is able to investigate their spin-polarized radioactive counterparts. One example of this is the study of the muon in semiconductors, where μ^{+} acts as a light pseudo-isotope of hydrogen [8–23]. Another example is the study of radioactive nuclei such as ^{12}B and ^{12}N in semiconductors [24–27]. In these techniques, the radioactive particle of interest is implanted into the material, and the time evolution of the spin polarization is monitored by detecting the decay β particle (e.g. electron or positron). Due to parity violation of β decay, the electron (positron) is emitted opposite (along) the direction of the particle's spin at the time of decay.

Recently, a β-detected nuclear magnetic resonance (β-NMR) facility has been constructed at TRIUMF in Vancouver. This facility can be used to study the behavior of isolated, highly polarized ^{8}Li (spin 2 nuclei and lifetime $\tau = 1.2$ s) impurities in bulk and nano-scale condensed matter systems, including semiconductors. Currently only ^{8}Li is being used, however, radioactive beams of different ions are under development. In the study of defects in condensed matter systems, it is important to determine the exact location of an impurity in the lattice and to understand the response of the environment to its presence. Such information can be obtained using the so-called cross-relaxation (CR) technique, which is also known as level-crossing resonance (LCR) and avoided level crossing (ALC) in the literature [17].

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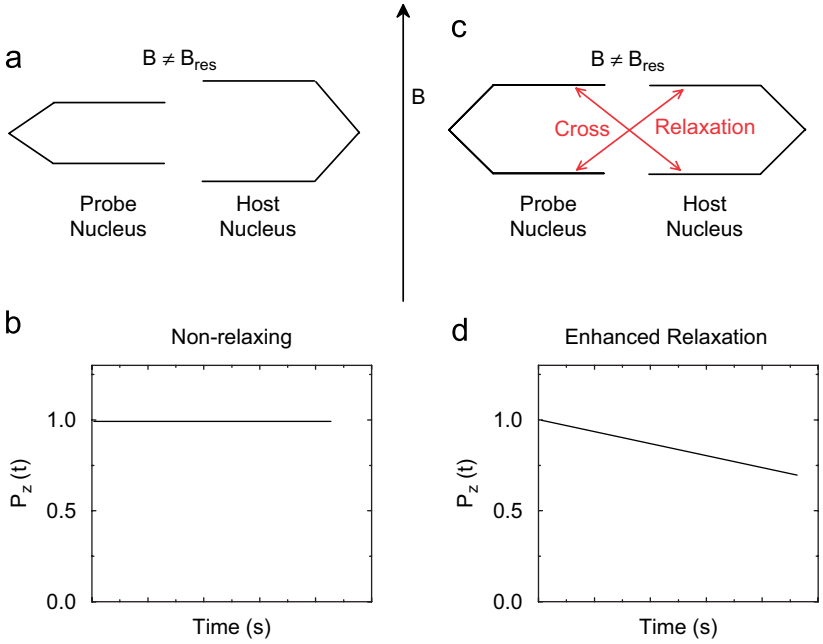

Fig. 1. Qualitative picture showing the principle of the cross-relaxation technique. (a) An applied magnetic field far from resonance results in non-relaxing polarization of the probe spin as shown in (b). At resonance field $\mathbf{B}_{res}$ (c) the cross relaxation is triggered resulting in a transfer of polarization from the probe spin to the host spin, this is observed as enhanced relaxation of the probe spin polarization as shown in (d).

In this paper, we present a description of the development of the CR technique using the β-NMR facility with ^{8}Li. In particular, we discuss the recent implementation of the CR technique in a ⟨1 1 0⟩ single crystal of the face-centered cubic metal Cu. Being one of the simple elemental fcc metals with nuclear spin $\frac{3}{2}$ and a relatively large quadrupole moment, Cu is one of the best candidates to start the development of the CR technique. Moreover, the CR effects have been already observed for muons [28] and radioactive ^{12}B [29] in Cu. We expect that this technique will have many applications beyond simple metals, especially in the studies of defects in semiconductors.

2. Principles of CR

The principle of the CR method lies in the interaction between the $^{8}Li^{+}$ probe and its host in an external magnetic field [30,31]. Once inside the sample, $^{8}Li^{+}$ can interact with its host via Li-nuclear dipole–dipole and Li-induced quadrupole (if the host nuclei have spin $\geqslant 1$) interactions. The induced quadrupole interaction is due to the non-zero electric field gradient (EFG) created by the ^{8}Li impurity on its neighboring host nuclei. Applying an external magnetic field to the $^{8}Li^{+}$-host system varies the energy levels of both the ^{8}Li and host nuclei (Zeeman effect). At certain resonant values of the applied field, $\mathbf{B}_{res}$, the energy level splittings of ^{8}Li match those of the neighboring host nuclei. In this situation energy exchange between the implanted probe and its neighboring nuclei is possible enabling spin flip–flop processes, and consequently an enhanced relaxation rate of the implanted probe polarization. A schematic picture of the split energy levels in off/on resonance case is shown in Fig. 1(a) and (c), respectively, with the corresponding polarization as a function of time is shown in Fig. 1(b) and (d). Hence, a measurement of the relaxation rate (λ) of the probe polarization as a function of the applied field yields a measure of the different values of $\mathbf{B}_{res}$, which in turn provides valuable information about the nature and strength of interaction between the probe (i.e. the isolated impurity) and the host nuclei.

3. Experimental details

The experiment was performed at the Isotope Seperator and Accelerator (ISAC) β-NMR facility at TRIUMF in Vancouver, Canada. A beam of radioactive $^{8}Li^{+}$ is generated in the ISAC target and delivered to the β-NMR facility. A high degree of nuclear polarization (~70%) is generated inflight using a collinear optical pumping method. The beam is then implanted into the sample at a rate of about 10^{6}/s. The β-NMR spectrometer sits on a high voltage platform allowing us to change the implantation energy of the ^{8}Li between 1 and 30 keV. This enables us to control the implantation depth of the probe into the bulk of the sample down to nm scale [32]. When the $^{8}Li^{+}$ decays it emits a high energy (~6 MeV) β electron preferentially in a direction opposite to its spin direction (z-axis in our case) at the time of decay. The emitted βs are detected by two fast plastic scintillation detectors: forward (F) and backward (B). The $^{8}Li^{+}$ spin polarization P_z is proportional to the asymmetry A in the counting rates: $A = (F + B)/(F - B)$. In CR we implant the beam for a period $T = 4$ s and monitor the time dependence of the

$^8Li^+$ polarization $P_z(t)$ by measuring the β-decay asymmetry both during and after the beam period [33,34].

The external magnetic field **B** was applied along the ⟨1 1 0⟩ axis of the 99.999% pure Cu single crystal (Accumet Materials Company) and parallel to the $^8Li^+$ spin polarization direction. The sample, which is 1 mm thick, has one polished surface with an area of $8 \times 10\,mm^2$ facing the beam. The polished surface was prepared by subsequent sputter cleaning and UHV annealing at the Surface Physics Lab in Simon Fraser University after which the sample was capped with a thin Au layer to prevent surface oxidation. A β-NMR experiment [35] on a Cu-thin film has already been carried out, where the positive Knight shifts and spin relaxation data show that $^8Li^+$ occupies a substitutional site (S-site) at temperatures close to room temperature. Relying on that, we performed our experiment at room temperature.

4. Results and discussion

The time dependence of the $^8Li^+$ polarization $P_z(t)$ is determined by both the $^8Li^+$ spin–lattice relaxation rate and its radioactive lifetime $\tau = 1.21$ s. Assuming a general spin relaxation function $f(t, t_p; \lambda)$ for the fraction of $^8Li^+$ implanted in the sample at time t_p, the polarization follows [34]:

$$f(n) = \begin{cases} \dfrac{\int_0^t e^{-(t-t_p)/\tau} f(t, t_p; \lambda)\, dt_p}{\int_0^t e^{-t/\tau}\, dt}, & t \leqslant T, \\ \dfrac{\int_0^T e^{-(T-t_p)/\tau} f(t, t_p; \lambda)\, dt_p}{\int_0^T e^{-t/\tau\, dt}}, & t > T, \end{cases} \quad (1)$$

where $f(t, t_p; \lambda)$ has a phenomenological exponential form

$$f(t, t_p; \lambda) = A e^{-\lambda(t-t_p)}. \quad (2)$$

By fitting the raw data to Eq. (1) we were able to extract the $^8Li^+$ spin–lattice relaxation rate λ. Typical data of $P_z(t)$ in two different magnetic fields, 3500 and 3800 G, at room temperature is shown in Fig. 2. The solid curves are best fits to Eq. (1). The CR spectrum is shown in Fig. 3 which consists of the field dependence of the $^8Li^+$ spin–lattice relaxation rate λ at room temperature. The position of the peaks, magnified in the inset of Fig. 3, represents the resonance fields at which the transfer of $^8Li^+$ polarization to the host's spin (Cu in our case) are maximal. In Fig. 3 one can notice non-zero field independent contribution to λ far from resonance. Ideally there should be no such relaxation of the $^8Li^+$ polarization far from resonance since the $^8Li^+$ nucleus is in its eigenstate. Here, this relaxation is due to random spin–flip of the conduction electrons from the $^8Li^+$ nucleus, i.e. Korringa relaxation (for more details consult Ref. [32]). Another noticeable feature is the enhanced relaxation at magnetic fields close to zero. This enhancement is due to the matching between the energy level splittings of ^8Li and the host nuclei at low field, that is, a zero crossing resonance. This behavior is

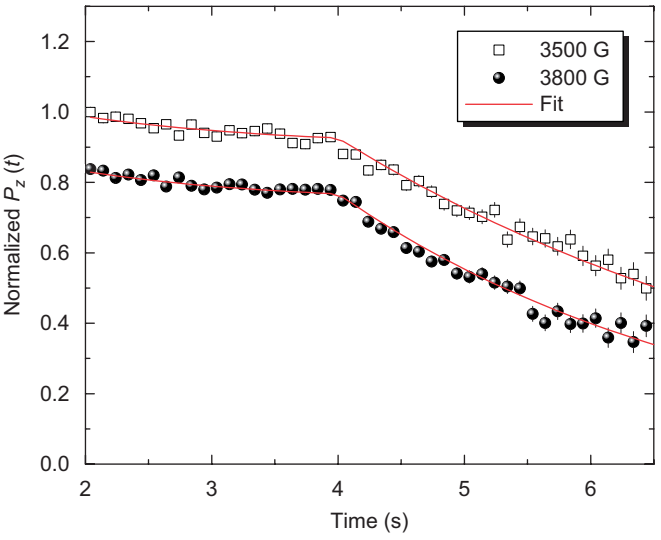

Fig. 2. Typical raw data of the time dependence of $^8Li^+$ polarization under two different applied magnetic field, 3500 and 3800 G. The solid curves are best fits to Eq. (1).

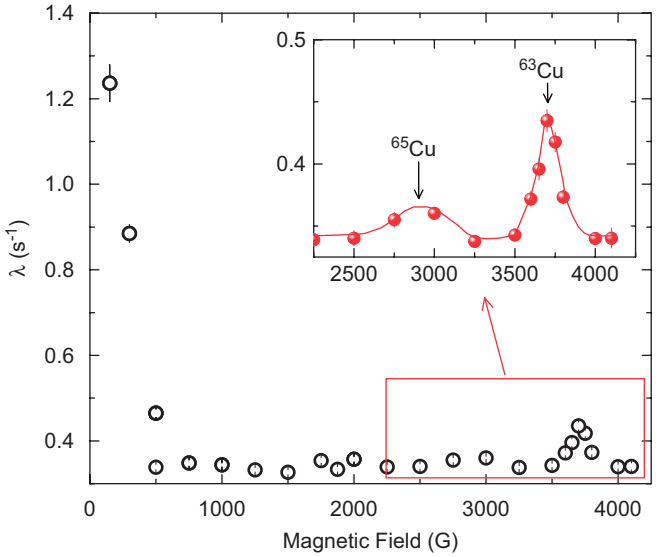

Fig. 3. Cross-relaxation spectrum showing the field dependence of $^8Li^+$ spin–lattice relaxation rate λ. The inset is a magnified plot of the resonant peaks explained in the text (the solid curve is a guide to the eye).

observed in all materials whose nuclei have dipole moments (although the amplitude of this relaxation would be different due to the difference in the dipole moments between these materials).

In the CR resonances shown in the inset of Fig. 3, there are two peaks due to the two Cu isotopes ^{63}Cu and ^{65}Cu. The relative natural abundance of each isotope, which gives the ratio of the relative amplitudes of their resonant peaks, enabled us to identify which peak corresponds to which isotope. Moreover, the relative positions of the two peaks can be unambiguously determined from the quadrupole and dipole moments of ^{63}Cu and ^{65}Cu. In order to establish the occupation site of the $^8Li^+$ in the fcc Cu

lattice, e.g. whether it is the substitutional site as proposed by Oshumi et al. [36] or not, using our CR technique, we need to go to higher magnetic fields and search for more resonances.

Although preliminary, these results demonstrate that it is indeed possible to conduct CR experiments on $^{8}Li^{+}$ in solids. This will likely develop into a promising technique for investigating $^{8}Li^{+}$ impurities in semiconductors [24].

5. Summary

In summary, we presented a report on the development of the cross-relaxation method and its application for studying ^{8}Li in a Cu ⟨1 1 0⟩ single crystal. It is anticipated that this method will provide detailed information that will improve the understanding of the microscopic properties of impurities in semiconductors and other condensed matter systems.

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