Longitudinal-Field μ^+ Spin Relaxation via Quadrupolar Level-Crossing Resonance in Cu at 20 K

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(Received 5 March 1985)

We report the first detection of resonant longitudinal-field μ^+ spin relaxation via dynamic depolarization at a level-crossing resonance between the μ^+ Zeeman splitting and the induced quadrupolar coupling of the muon's nearest-neighbor nuclei. The μ^+ relaxation rate as a function of external magnetic field B has a peak at the level-crossing resonance. In single-crystal Cu at 20 K with the [111] axis parallel to **B** the resonance occurs at a field of $B_{\text{res}} = 80.9 \pm 0.4$ G with a FWHM of 21.7 ± 1.7 G. This approach should help clarify the controversial low-temperature motion of the μ^+ in Cu.

PACS numbers: 76.90.+d, 76.60.Es, 76.60.Gv

Positive-muon spin rotation/relaxation is the name given collectively to a variety of experimental methods utilizing the parity-nonconserving decay of 100% spin-polarized muons as a means of probing chemical and condensed-matter physics.[1–6] As with any new discipline, the repertoire of techniques utilized in muon spin relaxation is relatively limited compared with that of a long-established field such as NMR.[7,8] In particular, a resonance spectroscopy like NMR offers the resourceful investigator the freedom to focus on any chosen part of the interaction Hamiltonian.[9] Pursuing the need to establish a similar variety of methods in muon spin relaxation, we have tested one of the well-known solid-state level-crossing (or "cross relaxation") methods commonly used in NMR[10,11]: For muons in metals one can establish a level-crossing resonance (LCR) between the Zeeman interaction of the μ^+ spin **S** in an external magnetic field **B** and the quadrupolar interaction of the ith neighboring host nucleus with spin $I^i > \frac{1}{2}$. In an unstressed Cu crystal the quadrupolar coupling itself arises from the presence of the μ^+ and its attendant electronic and/or lattice distortions, which locally destroy the cubic symmetry of the surrounding host lattice. The observed phenomenon is an enhanced muon spin depolarization rate Λ at the resonant field B_{res}.

Relaxation mechanisms for the μ^+ in nonmagnetic hosts arise primarily from H_D, the dipolar Hamiltonian[7,8] between the μ^+ spin **S** and the neighboring Cu spins $\mathbf{I}^i$, with subsequent motional effects superimposed. Other interactions, such as electronic Korringa relaxation or motionally induced high-field spin-lattice terms,[7,8] are generally slow with respect to the 0.454-μs^{-1} decay rate of the muon and rarely, if ever, have observable effects.

In LCR muon spin relaxation one utilizes muons initially polarized *along* **B** and, by adjusting the field strength, matches the energy splitting of the muon's Zeeman levels to that of the magnetic levels of the host nuclei, which are determined mainly by their quadrupolar energies. Such an energy-splitting match is equivalent to the Hartmann-Hahn resonance condition of NMR.[11] In terms of frequencies, the resonance condition is roughly $\omega_Z^\mu \simeq \omega_Q$, where ω_Z^μ is the muon Larmor frequency and ω_Q is $1/\hbar$ times the magnitude of the difference between nuclear quadrupole energy levels. In terms of magnetic field, this means $B_{\text{res}} \simeq \omega_Q/\gamma_\mu$, where $\gamma_\mu = 0.085\,14$ rad μs^{-1} G^{-1} is the muon's gyromagnetic ratio.

Within a linewidth of B_{res}, that part of the dipolar Hamiltonian H_D containing energy-conserving "flip-flop" terms $H_D'^i$ proportional to $(S_+ I_-^i + S_- I_+^i)$ will mix the muon spin-up and spin-down eigenstates, resulting in an observable muon spin depolarization together with an unobserved growth in the polarization of the nuclear levels associated with the LCR.[12] If B is far from B_{res} (on the scale of $H_D'^i/\hbar\gamma_\mu$), the muon-nuclear transitions no longer conserve energy and the depolarizing effect of level mixing is inhibited. For positive muons in Cu this "accidental" degeneracy at the LCR reduces the characteristic μ^+ spin-lattice relaxation time T_1 from its Korringa value of 0.01–1 s (for typical metal hydrides at low temperatures)[13] down to the order of the static rigid-lattice transverse relaxation time, 10^{-6}–10^{-4} s.

In the present experiment, a single crystal of Cu (the same as used by Clawson[14]) was placed in a horizontal cold-finger cryostat into which a beam of 4-MeV "surface muons"[5] entered axially through a thin Mylar window and heat shield at one end. A longitudinal magnetic field B of 0–4000 G could be applied along the beam direction (parallel to the muon spins). The Cu crystal was mounted with a [111] crystal axis parallel to $\mathbf{B}$. The measuring temperature of 20 K was chosen to be close to the observed minimum of the muon hop rate in Cu.[6]

Positrons from μ^+ decay were detected in forward (F) and backward (B) scintillation counters and the time distributions $F(t)$ and $B(t)$ of such events relative to the muon's entry into the target at $t=0$ were collected in a computer in the conventional way.[1-6] Time-independent backgrounds were determined for $F(t)$ and $B(t)$ from negative-time bins (obtained by delaying all positron triggers) and subtracted from each to form $F'(t)$ and $B'(t)$. The corrected time spectra were then combined to form the raw asymmetry spectrum

$$A'(t)=[B'(t)-F'(t)]/[B'(t)+F'(t)], \tag{1}$$

which was finally converted to the corrected asymmetry spectrum

$$A(t)=\frac{(1+a)A'(t)-(1-a)}{(1+a)-(1-a)A'(t)}, \tag{2}$$

where $a=N_F^0/N_B^0$ is the ratio of F to B counting efficiencies.

Since $A(t)=A_0G(t)$ is proportional to the muon ensemble polarization $G(t)$ as a function of time, the fitting of $A'(t)$ involved only two normalization parameters *not* related to muon relaxation: the uninteresting systematic parameter N_F^0/N_B^0 and the empirical full asymmetry A_0. The latter was determined from the zero-field (ZF) spectrum, which had the familiar form[14,15] of a Gaussian Kubo-Toyabe relaxation function $A(t)=A_0G_{zz}^{\mathrm{KT}}(t)$, with $A_0=0.261(3)$, a static linewidth $\Delta=0.295(6)$ μs^{-1}, and a small hop rate. In the global fit of the longitudinal-field (LF) spectra, A_0 was held fixed at the above value—although strong magnetic fields can alter e^+ orbits and the effective full asymmetry, this is a very small correction below 100 G, where these data were taken. A more common systematic effect due to weak longitudinal fields is the loss of efficiency in selected counters, affecting N_F^0/N_B^0, which is also susceptible to small fluctuations with beam intensity, etc. This parameter was therefore allowed to vary freely for each spectrum.

Leaving a detailed comparison with the quantum dynamics for a future publication, we have chosen to parametrize the muon-spin-relaxation function $G(t)$ in the phenomenological form

$$G(t)=\exp[-(\Lambda t)^{\beta}], \tag{3}$$

simply because it empirically succeeds in describing the observed decay of the asymmetry in all the runs near the LCR with a common value of $\beta=1.27(5)$, as can be seen for selected values of B in Fig. 1. This treatment yields relatively model-independent values of the relaxation rate Λ, the inverse of the apparent time T_1 required for the initial polarization to decrease by a factor of $1/e$. The results of the analysis are shown in Fig. 2 as $\Lambda(B)$.

The muon-spin-relaxation level-crossing resonance shown in Fig. 2 is centered at $B_{\mathrm{res}}=80.9(4)$ G and is well fitted by a Gaussian shape with a width of $\delta B=13(1)$ G (i.e., a FWHM of 21.7 ± 1.7 G). The

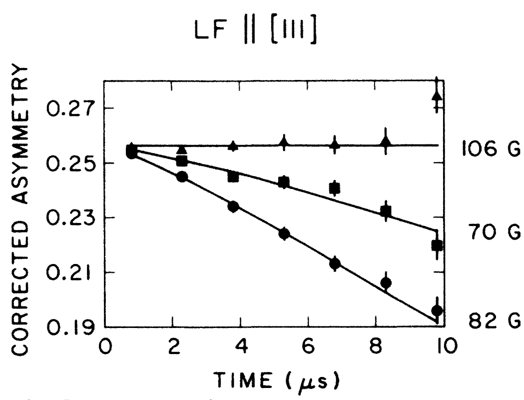

FIG. 1. Longitudinal-field muon-spin-relaxation asymmetry spectra [proportional to the muon polarization $G(t)$ parallel to the applied field] for several fields (circles, 82 G; squares, 70 G; triangles, 106 G) near the level-crossing resonance in Cu at 20 K. The lines through the points are best fits according to Eq. (3). Note the suppressed zero on the vertical scale.

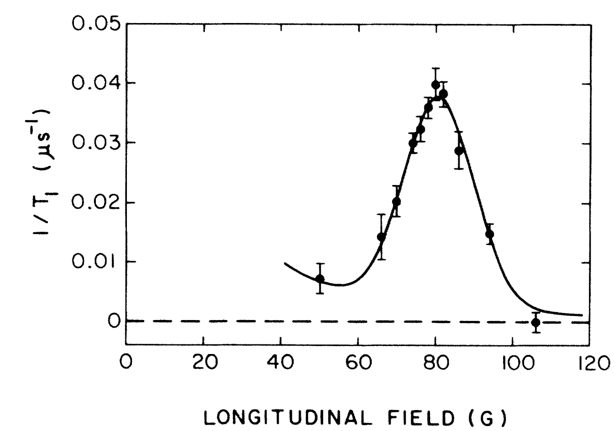

FIG. 2. Longitudinal-field muon-spin-relaxation level-crossing resonance in a Cu crystal at 20 K with [111] axis parallel to the external magnetic field $\mathbf{B}$. The line through the points is a fit with a Gaussian lineshape on top of a background decreasing as B^{-2} (see text).

maximum relaxation rate due to the LCR effect is $\Lambda(B_{res}) = 0.035(1)\ \mu s^{-1}$. One may think of $\Lambda(B_{res})$ as resulting from an oscillating effective field of magnitude $B_{eff} = \Lambda/\gamma_\mu \simeq 0.43$ G due to the Cu moments precessing in their respective electric field gradients at the muon Larmor frequency. This quantity can be compared with a mean static random local field $\Delta/\gamma_\mu \simeq 3.6$ G in the Kubo-Toyabe model.

As can be seen from Fig. 2, the resonance peak is not perfectly symmetric. Its asymmetry is characterized by an underlying background relaxation rate $\Lambda_0(B)$ caused partly by the slow hopping of the μ^+ at 20 K in a weak longitudinal field. As is well known,[5,6,14,15] there is no persistent relaxation in longitudinal field for $B \gg \Delta/\gamma_\mu$ as long as the μ^+ is truly static. However, in the presence of a small but finite hop rate ν, the effective relaxation rate Λ_0 goes through a maximum (corresponding to a T_1 case is far below the LCR resonance at B_{res} and even below Δ/γ_μ. Following standard theory,[16] we fitted this contribution with a B^{-2} dependence.

The resonance shown in Fig. 2 displays qualitative features consistent with dynamical behavior governed by the Hamiltonian

$$H = H_Z^\mu + \textstyle\sum_i (H^i + H_D^{\prime i}), \tag{4}$$

where $H_Z^\mu = \hbar\gamma_\mu(\mathbf{S}\cdot\mathbf{B})$ is the muon Zeeman interaction and the index i labels neighboring Cu nuclei; $H^i = H_Q^i + H_Z^i$, where $H_Z^i = \hbar\gamma_{Cu}(\mathbf{I}^i\cdot\mathbf{B})$ and $H_Q^i = \frac{1}{2}\hbar\omega_Q^i[I_z^{i2} - \frac{1}{3}I^i(I^i+1)]$ is axially symmetric with the quantization axis for the ith nucleus directed radially away from the assumed octahedral site of the muon. Note that this axis is not generally parallel to the applied field direction along which the Zeeman energy is quantized.[7] The eigenstates of H^i are denoted by $|+\frac{3}{2}\rangle$, $|+\rangle$, $|-\rangle$, and $|-\frac{3}{2}\rangle$, where the $|+\rangle$ and $|-\rangle$ states are linear combinations of the $|\pm\frac{1}{2}\rangle$ states whose degeneracy is lifted by H_Z^i. The LCR occurs when the muon's Zeeman splitting equals one of the four energy differences between the nuclear $|\pm\frac{3}{2}\rangle$ and $|\pm\rangle$ states, and is driven by the nearly energy-conserving terms $H_D^{\prime i}$, which connect only the above-mentioned states. The value of the "on resonance" relaxation rate is substantially reduced from the ZF value principally because the effective dipolar coupling $H_D' = \sum_i H_D^{\prime i}$ is only a small part of the full H_D.

The relaxation function $G(t)$ can be expressed as a power-series expansion[17] in terms of the "partial moments" M_n' of the "truncated" dipolar interaction H_D':

$$G(t) \simeq 1 - \frac{1}{2}M_2't^2 + \frac{1}{4!}M_4't^4 - \ \dots \tag{5}$$

This representation of $G(t)$ is not very helpful in fitting the data of Fig. 1, but allows a simple theoretical interpretation of the LCR line shown in Fig. 2. The second moment can be shown to have a constant value $M_2' = 3\omega_D^2$, with $\omega_D = \gamma_\mu\gamma_{Cu}/r^3$, r being the μ^+-Cu distance. This is to be compared with the ZF M_2 of $24\omega_D^2$, which is twice the value of the Kubo-Toyabe Δ^2 commonly associated with ZF relaxation of muons in Cu.[18,19]

Since M_2' is constant, the effective Λ is a maximum when M_4' is a minimum; this defines the resonant field B_{res}. Recognizing that the largest nontrivial contribution to M_4' comes from the term H_Z^i, we find that

$$M_4'(B) \simeq \{[\omega_Q + (\gamma_\mu - \gamma_{Cu})B]^2 + (\omega_Q + \gamma_\mu B)\gamma_{Cu}B\}\omega_D^2.$$

Minimizing with respect to B yields $B_{res} \simeq (1 + \frac{1}{2}\gamma_{Cu}/\gamma_\mu)\omega_Q/\gamma_\mu$ to first order in γ_{Cu}/γ_μ. Thus B_{res} is fractionally higher by about $\frac{1}{2}\gamma_{Cu}/\gamma_\mu$ than the value of $\omega_Q/\gamma_\mu \simeq 76$ G previously deduced by Camani *et al.*,[20] using the formulation of Hartmann.[21]

Two terms in the Hamiltonian influence the width and shape of the resonance curve: H_Z^i and $\sum_i H_Q^i$. The effect of the first term can be estimated by calculation of the FWHM of $M_4'(B)$. The latter term arises from the binomial probability distribution of nearest-neighbor Cu isotopes with different quadrupole moments,[22] which should also make the line slightly asymmetric. The respective contributions to the FWHM are approximately $\delta_Z = 1.0$ and $\delta_Q = 0.56$ rad/μs. The appropriate combination of these frequency shifts gives an effective width consistent with the observed value.

The introduction of this new muon-spin-relaxation method facilitates a number of very promising applications. Within a large class of materials including covalent and ionic insulators, semiconductors, and metals, the μ^+ either creates or (for noncubic materials) alters the electric field gradient at neighboring nuclei; measurements of the resulting values of ω_Q should provide new experimental tests of current theories of bonding and electronic structure.[23] Furthermore, the effects of each nonequivalent nucleus can be selected separately for study, because only those nuclei satisfying the LCR condition will appreciably relax the μ^+. For strong dipolar coupling, the μ^+ relaxation function near resonance reflects the specific configuration of those nuclei participating in the LCR. Of particular interest in muon spin relaxation is the case of muons trapped by impurities,[24] where these methods should provide a powerful impurity-specific probe.

We expect this technique to find further applications to the study of muon motion in solids. One may imagine a variety of narrowing and/or shifting behavior as the hopping rate becomes comparable with the dipolar coupling frequency ω_D and then with the LCR resonance frequency $\gamma_\mu B_{res}$ itself. Of particular interest will be the study of low-temperature μ^+ diffusion in Cu.[3,5,6,14,25,26] For example, the single-jump migration from octahedral to tetrahedral coordination proposed by Seeger and Schimmele[6] would result in a disappearance of the formerly resonant relaxation.

Finally, the availability of a well-known microscopic few-particle Hamiltonian is expected to be of great benefit in the calculation of realistic physical models.

We are most grateful to Professor A. Abragam for sending us his analysis of the potential of LCR methods in a private communication. We would also like to thank John Worden of the TRIUMF muon-spin-relaxation group for developing special resonance-scanning software on short notice. This research was supported by the Natural Sciences and Engineering Research Council of Canada and, through TRIUMF, by the Canadian National Research Council.

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