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Muon level-crossing resonance in antiferromagnetic MnF_2

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We report the observation of a muon-nuclear level-crossing resonance (LCR) in the antiferromagnet MnF_2. The resonance occurs when the spin transition frequency of an interstitial muon is matched to that of the nearest-neighbor ^{19}F nuclei, allowing for a resonant transfer of polarization from the muon to the nuclei. The applied external field H_0 at which the LCR occurs is a measure of the local magnetic field on the neighboring ^{19}F nuclei. The observed shift relative to earlier ^{19}F NMR results is attributed to the disturbing influence of the muon. A second resonance is observed when H_0 cancels the longitudinal component of the local field at the muon.

Muon and muonium defect centers in solids are novel types of impurities whose electronic structure is the same as that of hydrogen, except for small zero-point motion effects resulting from the fact that the muon has about $\frac{1}{9}$th the mass of a proton. Although double-resonance techniques such as electron-nuclear double resonance (ENDOR) have been used for many years to characterize the electronic structure of pointlike impurities such as hydrogen, it is only recently that similar techniques have been applied in muon spin rotation (μSR). Since the application of level-crossing resonance (LCR) spectroscopy to μSR was first proposed by Abragam,[1] experiments in copper,[2] muonated radicals,[3,4] and semiconductors[5] have demonstrated the utility of the method for determining the hyperfine and/or electric quadrupolar parameters of the neighboring nuclear spins.

In this paper we report the first application of LCR in a magnetically ordered material; the antiferromagnet MnF_2. Two resonances have been observed below the Néel temperature $T_N = 67.336$ K. One occurs at a field where the muon spin transition frequency is matched to that of the two nearest-neighbor ^{19}F nuclei. A shift in the position of this resonance relative to the one predicted using NMR results on ^{19}F is attributed to the disturbing influence of the muon. A second resonance occurs when H_0 cancels the longitudinal component of the local field at the muon. These results indicate that LCR can provide new spectroscopic information on muon defect centers in magnetically ordered materials, which will be useful in understanding the electronic structure of hydrogenlike impurities in such materials and might facilitate the use of the muon as a probe of magnetism of solids.

De Renzi *et al.*[6] have previously investigated positive muons in CoF_2 and MnF_2, which have the rutile crystal structure. In CoF_2 a single muon procession frequency was observed below T_N(37.85 K), corresponding to a local field (at $T = 0$ K) of 0.2288(1) T, which is aligned with the $\hat{c}$ axis. They concluded that the signal was due to a muon localized at the octahedrallike interstitial site which, in an undistorted lattice, has two nearest-neighbor and four next-nearest neighbor ^{19}F nuclei 1.5 times more distant. This site assignment is consistent with an $F:\mu^+:F$ hydrogen-bonded center which has recently been observed in a variety of ionic fluoride crystals,[7] including ZnF_2, which is isostructural with MnF_2 and CoF_2.

In MnF_2 De Renzi *et al.* could detect no precession signal below T_N, whereas above T_N a single precession signal was found with an amplitude corresponding to about $\frac{1}{3}$ of the muon polarization. The orientation dependence of the field-induced fine structure was consistent with, but not unique to, the same octahedrallike site proposed for muons in CoF_2. More recently, two muon precession frequencies have been observed below T_N in MnF_2 in zero applied magnetic field (ZF) using a special high timing resolution spectrometer.[8] The frequencies extrapolated to $T = 0$ K (152 and 1280 MHz) correspond to local fields of 1.120 and 9.500 T, respectively, aligned with the $\hat{c}$ axis. The initial precession amplitudes indicate that the formation probabilities for the high- and low-frequency centers are in a ratio of about 2:1. The low-frequency center is most likely the one observed above T_N by De Renzi *et al.*[6] and the analogue of the muon center observed in CoF_2 (a muon situated at the octahedrallike interstitial site). The high-frequency center is thought to be muonium (u^+e^-).[8]

Muon-nuclear LCR's may occur at specific magnetic fields where there is a near degeneracy between two muon-nuclear hyperfine (hf) levels. In order for there to be observable effects on the muon polarization it is required that (1) the two levels have a different $\hat{z}$-component of muon spin and (2) there is a coupling (either a direct dipolar or indirect hyperfine interaction[9,10]) between the muon and nucleus which mixes the levels and lifts the degeneracy. LCR's involving the low-frequency center and the neighboring spin-$\frac{1}{2}$ ^{19}F nuclei are expected to occur in low fields because the hf levels involved are nearly degenerate, even in ZF, because of the closeness in the muon and ^{19}F frequencies (152 MHz for the muon versus 160 MHz for ^{19}F in an undistorted lattice[11]). On the other hand, LCR's involving the spin-$\frac{5}{2}$ ^{55}Mn nucleus, which has an NMR frequency of 671 MHz at $T = 0$ K,[12] are expected to occur at much higher fields and to be split by the nuclear electric quadrupolar interaction. In lowest order, neglecting effects due to bulk magnetic susceptibility, ^{55}Mn nuclear spins, and indirect hf coupling, the spin Hamiltonian for the low-frequency center in an applied field $\mathbf{H}_0$ may be expressed as

$$\mathcal{H}/h = \gamma_\mu(\mathbf{H}_\mu^{\rm loc}+\mathbf{H}_0)\cdot\mathbf{S} + \sum_i[\gamma_F(\mathbf{H}_i^{\rm loc}+\mathbf{H}_0)\cdot\mathbf{I}_i+\mathcal{H}_{\rm dip}^i/h] \;, \qquad (1)$$

where $\mathbf{S}$ and $\mathbf{I}_i$ are the spins of the muon and ith ^{19}F nuclei, $\mathbf{H}_{\mu,i}^{\rm loc}$ are the local fields acting on them, $\gamma_{\mu,F}(=2\pi\gamma_{\mu,F})$ are their gyromagnetic ratios, and $\mathcal{H}_{\rm dip}^i$ is the muon-^{19}F dipolar interaction. In the following analysis the local fields on the muon and ^{19}F nuclei are assumed to be aligned with the $\hat{c}$ axis.

There are basically three types of LCR's, which are shown schematically in Fig. 1, for a muon interacting with a single ^{19}F nucleus. On resonance a transition is allowed to occur between the two nearly degenerate hf levels,

$$(S_z,I_z)\rightarrow(S_z-1,I_z-\Delta+1) \;, \qquad (2)$$

where the quantity Δ (the difference between the total $\hat{z}$ component of spin of the two hf levels) may be used to characterize the LCR. The $\Delta = 0$ (or 2) LCR occurs at a field where one of the two muon transition frequencies is equal (or opposite) to that of the neighboring ^{19}F nucleus and involves a flip-flop (or flip-flip) of the muon and ^{19}F spins. The $\Delta = 1$ LCR occurs when H_0 cancels the longitudinal component of the local field on the muon, so that the muon is free to precess in the transverse component of the local field. Note that in this case there is no change in the ^{19}F spin. The magnetic fields at which these level-crossing resonances occur H_R^Δ are approximately given by

$$H_R^\Delta \cong [\gamma_\mu|\mathbf{H}_\mu^{\rm loc}| \pm (\Delta-1)\gamma_F|\mathbf{H}_F^{\rm loc}|] \times\cos\theta/[\gamma_\mu+(\Delta-1)\gamma_F] \;, \qquad (3)$$

where θ, the angle between the $\hat{c}$ axis and the applied field, is assumed to be small and the $\pm$ sign refers to the sign of $\mathbf{H}_\mu^{\rm loc}$ relative to $\mathbf{H}_F^{\rm loc}$.

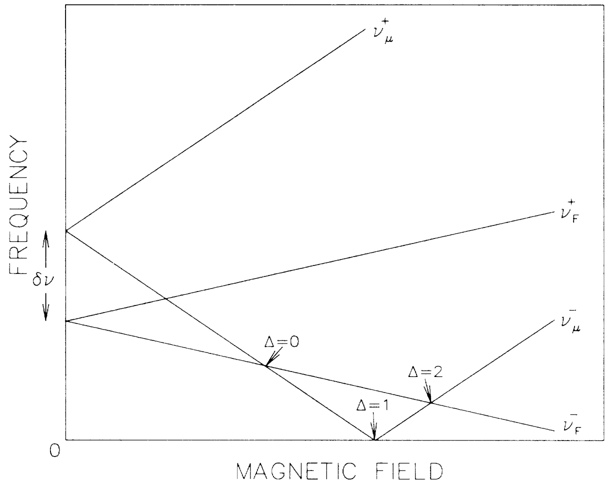

FIG. 1. Schematic of the magnetic field dependence of the precession frequencies for a muon and a single nearest-neighbor ^{19}F nucleus in an antiferromagnet. It is assumed that H_0 is parallel to the $\hat{c}$ axis and that the local field at the muon is parallel to that at the ^{19}F nucleus. The $\pm$ signs refer to the two possible magnetic sublattices. The positions of the level-crossing resonances are indicated.

The effect of a level crossing on the muon polarization may be estimated using degenerate perturbation theory. For an LCR involving a single spin-$\frac{1}{2}$ nucleus, the muon polarization in a longitudinal field near the resonance evolves in time according to[3,4]

$$P_z^\mu(\mathbf{H}_0,t) = \tfrac{3}{4} + \tfrac{1}{4}(\cos^2\beta+\sin^2\beta\cos 2\pi\nu t) \;, \qquad (4)$$

where

$$\nu = [\nu_{\rm res}^2+\nu_{12}^2(\mathbf{H}_0)]^{1/2} \;, \qquad (5a)$$

$$\sin\beta = \nu_{\rm res}/\nu \;, \qquad (5b)$$

with $h\nu_{12}(\mathbf{H})$ the field-dependent energy splitting between the two unperturbed energy levels, $|\varepsilon_1\rangle$ and $|\varepsilon_2\rangle$, which are nearly crossing, and $h\nu_{\rm res}$ is the energy splitting on resonance between the mixed levels due to the perturbing interaction. Note from Eq. (4) that on each of the resonances $\frac{1}{4}$ of the muon polarization is time dependent and there are two nearly identical $\Delta=1$ resonances corresponding to the two possible values of I_z.

Treating the muon-nuclear dipolar interaction and the transverse component of $\mathbf{H}_\mu^{\text{loc}}$ as the perturbation, the degeneracy is lifted in first order so that

$$\nu_{\text{res}} \cong \langle \varepsilon_1 | \mathcal{H} | \varepsilon_2 \rangle / h \ , \tag{6}$$

with the result

$$\nu_{\text{res}}^{\Delta=0} = -(\tfrac{1}{4})(1-3\cos^2\phi)\gamma_\mu \gamma_F h/r^3 \ , \tag{7a}$$

$$\nu_{\text{res}}^{\Delta=2} = (\tfrac{3}{4})\sin^2\phi\, \gamma_\mu \gamma_F h/r^3 \ , \tag{7b}$$

$$\nu_{\text{res}}^{\Delta=1} = \gamma_\mu |\mathbf{H}_\mu^{\text{loc}}| \sin\theta \pm (\tfrac{3}{2}) \sin\phi \cos\phi\, \gamma_\mu \gamma_F h/r^3 , \tag{7c}$$

where $\mathbf{r}$ is the muon-^{19}F internuclear vector and ϕ is the angle between $\mathbf{H}_0$ and $\mathbf{r}$. Note that there is a small splitting in $\nu_{\text{res}}^{\Delta=1}$ due to the dipolar interaction which is normally negligible. The inclusion of additional nuclei has no first-order effect on the LCR's, provided they are inequivalent so that the LCR's are well separated. If the nuclei are equivalent then many of the features of the LCR may change, except the central position.[4] For example, if there are two equivalent ^{19}F nuclei, $\nu_{\text{res}}^{\Delta=0,2}$ will be $\sqrt{2}$ times larger.

The most expedient method for finding LCR's is to scan the magnetic field while monitoring the integrated asymmetry in the positrons from muon decay. The theoretical line shape[4] in the absence of relaxation may be obtained by weighting Eq. (4) with a factor $\exp(-t/\tau_\mu)$ and integrating over time, where $\tau_\mu = 2.2\ \mu$s is the muon lifetime. One obtains a Lorentzian line as a function of magnetic field with a natural (full) linewidth

$$\Gamma_R^\Delta = 2[\nu_{\text{res}}^2 + 1/(2\pi\tau_\mu)^2]^{1/2} / [\gamma_\mu + (\Delta-1)\gamma_F] \ . \tag{8}$$

The experiment was performed on the *M*15 beamline at TRIUMF which provides a separated beam of nearly 100% polarized positive muons of average momentum 28.7 MeV/*c*. The incoming muons were detected with a thin scintillation counter detector before being stopped in a single crystal of MnF$_2$ (30 mm diam × 5 mm thick), held within a cold-finger cryostat. The positrons from muon decay were detected with a pair of large solid-angle scintillation counters. The magnetic field was applied approximately along the $\hat{c}$ axis and parallel to the initial muon polarization direction.

Figure 2 shows the LCR spectra for MnF$_2$ at various temperatures below T_N. The signal is defined in terms of the integrated muon decay asymmetry along the magnetic field direction $\mathcal{A}^\pm$, which is proportional to the muon polarization, time-averaged over the muon lifetime.[3] The ± sign refers to the direction of a small modulation field (±20 mT) which was used to average out systematic errors in the raw integrated asymmetry. The curves in Fig. 2 are fits to a theoretical difference signal, using either one or two Lorentzian lines. The positions of the resonances were observed to scale with T approximately, as does the sublattice magnetization $M_s(T)$.

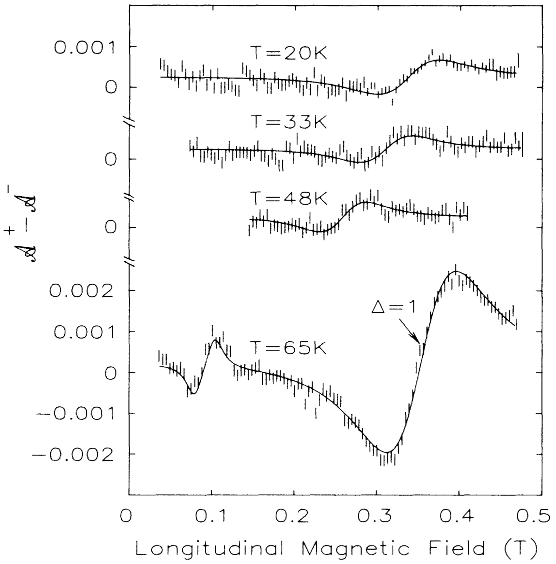

FIG. 2. The muon-^{19}F level-crossing spectra in MnF$_2$ as a function of temperature below T_N (67.336 K). The upper resonance at 65 K is off the scale at lower temperatures.

We attribute the upper resonance (seen only in the 65-K spectrum in Fig. 2) to a $\Delta=1$ LCR transition involving a flip in the muon spin with no change in the nuclear spins. The position of the resonance at 0.354(1) T is close to $|\mathbf{H}_\mu^{\text{loc}}| = 0.325$ T; the latter determined from a measurement of the muon precession frequency in ZF at approximately the same temperature. The difference is attributed to a small temperature shift of about 0.3 K between the two measurements. This assignment of the resonance is confirmed by the magnitude of the resonant oscillation ($\nu_{\text{res}} = 6.25$ MHz), which was measured using a standard time differential method. This is too large for either dipolar interaction or an indirect hyperfine coupling. However, it can be explained by a small transverse component of the local field equal to 0.046 T, arising from a misalignment of 7° between the $\hat{c}$ axis and the applied field [see Eq. (7c)]. The misalignment was confirmed after completion of the experiment using a birefringence technique. The measured width of the LCR [0.142(2) T] is larger than expected from Eq. (8) ($\Gamma_R^{\Delta=1} = 0.092$ T). This may be caused by inhomogeneous broadening of the muon transition frequency, which is discussed below. This type of LCR offers a new method for determining the local field on the muon and may be particularly useful when there is a distribution of such fields or when the signal is rapidly relaxing.

The lower resonance, seen at all temperatures in Fig. 2, is attributed to a $\Delta=0$ (or 2) LCR transition involving hf levels in which both the muon and the neighboring ^{19}F nuclear spins flip or flop. After taking into account the alignment of the crystal, the position of the lower LCR extrapolated to $T=0$ K [0.350(2) T] corresponds to a value of $\delta\nu = \pm 33.4(2)$ MHz or $\pm 61.4(4)$ MHz, where $\delta\nu$ is the difference between the muon and ^{19}F frequencies in ZF at $T=0$ K ($\delta\nu = +8$ MHz in an undistorted lattice). It is more likely that $\delta\nu = \pm 33.4(2)$ MHz since this is the solution of Eq. (3) when the local field on the muon and nearest neighbor ^{19}F are in the same direction. In order to completely remove the above ambiguity it would be necessary to resolve the other muon-nuclear LCR corresponding to $\Delta=2$ (or 0). A search for this resonance up to 3.0 T has been made, but the result was inconclusive,[13] indicating that the resonance may be even broader than the LCR already observed.

In spite of this uncertainty it is interesting to compare the possible values of the nearest-neighbor ^{19}F frequency with that determined from NMR. One finds the shift to be either -43%, -26%, $+16\%$, or $+33\%$, relative to the undisturbed lattice value of 160 MHz. This is reasonable considering that the muon breaks the local symmetry of its neighboring ions and thereby may distort both the local electronic structure and the positions of the neighboring ions. For example, the observed shifts can be explained by a change of a few percent in the Mn-F nearest-neighbor distance,[14] which in an undisturbed lattice has an average value of 2.12 Å. This high sensitivity to lattice constant comes primarily from the transferred hf contribution to the ^{19}F local field.[14] Such a distortion is reasonable if one assumes that a F:μ^+:F hydrogen-bonded center[7] is formed, in which the muon-F distance would be decreased from an undistorted value of 1.764 Å for muons at the octahedral-like site to ~ 1.21 Å. The Mn-F separation is probably altered to a lesser extent because (1) the muon-F internuclear direction is almost perpendicular to that for Mn-F and (2) the nearest-neighbor Mn ion positions might relax so as to approach the undistorted Mn-F separation.

The observed linewidths for the low field resonance shown in Fig. 2 are larger than the natural linewidth expected from the nuclear dipolar interaction [Eqs. (7) and (8)], although the integrated amplitude is consistent with just dipolar coupling between the muon and ^{19}F. Muons at the interstitial octahedral site have two nearest-neighbor ^{19}F nuclei for which the internuclear vector is perpendicular to the $\hat{c}$ axis, and thus have $\phi = 90° - \theta$ in Eq. (7). For a F:μ^+:F center $\gamma_\mu \gamma_F h/r^3 \cong 0.20$ MHz.[7] After taking into account that there are two equivalent nuclei, one obtains from Eq. (8) a resonant oscillation either $\nu_{\rm res}^{\Delta=0} = 0.056$ MHz or $\nu_{\rm res}^{\Delta=2} = 0.197$ MHz. Substituting these values into Eq. (8) yields a natural linewidth of $\Gamma_R^{\Delta=0} = 1.9$ mT or $\Gamma_R^{\Delta=2} = 2.4$ mT. The measured linewidth is an order of magnitude larger than these estimates and is also temperature dependent, scaling approximately with $M_s(T)$. It is interesting to note that in ZF the linewidth of the precession signal of the low-frequency center is also much larger than expected from T_1 measurements and has a similar temperature dependence.[8] This suggests that the LCR linewidth may be due to inhomogeneous broadening of the muon transition frequency. The origin of this broadening is not known.

In conclusion, we have demonstrated that level-crossing spectroscopy can be used to obtain information both on the local field at the muon and neighboring nuclear spins in magnetically ordered systems. This new technique should lead to an improved understanding of hydrogenlike defects in magnetic materials.

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