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Observation of muon-fluorine "hydrogen bonding" in ionic crystals

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We have found that a positive muon (μ^+) implanted into LiF, NaF, CaF_2, or BaF_2 pulls two F^- ions together in a strong "hydrogen bond" until the ^{19}F nuclei are separated by roughly twice the nominal F^- ionic radius, with the μ^+ midway between. The resultant "FμF" center is easily observed via the distinctive behavior of the collinear $^{19}F:\mu^+:^{19}F$ spin system (coupled by dipole-dipole interactions between the muon and the fluorine nuclei) in both transverse-field muon-spin rotation and zero-field muon-spin relaxation experiments. We speculate that implanted H^+ ions may initially form similar hydrogen bonds between adjacent F^- ions in many metal fluoride crystals.

The behavior of the positive muon (μ^+) implanted in alkali halide crystals has been studied for more than a decade, both theoretically[1-3] and experimentally[4-7] by means of muon-spin rotation relaxation resonance (μSR) techniques.[8] However, most previous work has focused on the paramagnetic muonium (μ^+e^- or Mu) center, which is formed by a fraction f_{Mu} of the muons. For example, recent high-field experiments[5] have revealed that Mu forms the equivalent of a hydrogenic U_2 center (a neutral atom in the tetrahedral interstitial location) in virtually all alkali halides, while muon-resonance experiments[6] have shown that Mu undergoes a thermal transition to a diamagnetic state (which could be μ^+, a Mu^- ion, or a covalently bonded Mu atom) in NaCl, KCl, and KI. In all those experiments it was recognized that a separate fraction f_d of the muons thermalize initially in a diamagnetic state,[7] whose time evolution has not been subjected to much scrutiny until now.

We report here the first detailed μSR investigation of this "prompt" diamagnetic fraction in fluoride crystals. The results reported here are of interest for two reasons: First, the solid-state chemistry of the μ^+ mimics that of an implanted proton or deuteron,[8] so that the evidence to be presented for the ubiquitous formation of a "hydrogen bond" between two F^- ions can be taken to apply to all hydrogen isotopes in metal fluoride crystals. Second, the dynamics of the simple spin system $^{19}F:\mu^+:^{19}F$ formed by the spin-$\frac{1}{2}$ muon and two spin-$\frac{1}{2}$ ^{19}F nuclei (henceforth denoted FμF) beautifully illustrates the limitations of classical Kubo-Toyabe (KT) treatments[9,10] of the relaxation of the muon-spin·polarization by nuclear dipoles; KT model functions have been widely used in a large program of condensed matter μSR research on the location, diffusion, and trapping of μ^+ and Mu (as light counterparts of the proton and the hydrogen atom, respectively) that depend upon the correct interpretation of muon-relaxation phenomena.[8,11,12]

In this typical time-differential μSR experiment[8] the separated beam of 4.1-MeV surface muons[13] from the M15 channel at TRIUMF was stopped in single crystals of LiF or NaF (rocksalt structure) or CaF_2 or BaF_2 (fluorite structure) situated in a He-gas-flow cryostat with thin windows. The $\langle100\rangle$ axes of the crystals were aligned parallel to the incident beam direction. As the orientation of the other axes was known only for the NaF sample, additional orientations were studied in that case, as described below.

The μ^+ spin ensemble is initially 100% polarized in the direction opposite to the muon beam. Subsequently, the μ^+ polarization $\mathbf{P}^\mu$ precesses in and/or is relaxed by interaction with magnetic fields, either applied externally or due to, e.g., the dipole moments of the host nuclei. This time dependence is manifest in the anisotropy of the positrons emitted from $\mu^+ \rightarrow e^+\nu\bar{\nu}$ decay,[8] which are detected as a function of time in backward (B) and forward (F) scintillation counters, where the directions described are relative to the muon-beam momentum. 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 and later combined to form an "asymmetry" spectrum $A(t)$ by conventional algorithms.[8,12] The initial asymmetry $A(0)$ reflects the fraction $f_d = A(0)/A_0$ of muons thermalizing at $t=0$ in a diamagnetic state; the "full-asymmetry" value $A_0 = 0.322(2)$ was determined from a control experiment on a high-purity Al foil target, in which there is negligible polarization loss.[8]

It is conventional to have $\hat{z}$ represent the direction of the external applied field, $\mathbf{H}_0 = H_0\hat{z}$. In zero applied field (ZF) or in a longitudinal field (LF), $\hat{z}$ is also the direction of $\mathbf{P}^\mu(0)$, and one is mainly concerned with $G_z(t)$, the longitudinal relaxation function, obtained by simply monitoring the time dependence of P_z^μ via $A(t)$: $G_z(t) = A(t)/A(0)$. In transverse field (TF), $\mathbf{P}^\mu(0)$ defines the x direction, and the resulting precession of the muon polarization in the xy

plane decays with a transverse relaxation function $G_{xx}(t)$:

$$A(t) = A(0)G_{xx}(t)\cos(\omega_\mu t + \phi) \ ,$$

where $\omega_\mu = \gamma_\mu H_0$ and $\gamma_\mu = 8.5137 \times 10^4$ s^{-1}Oe^{-1}. When several precession frequencies ω_l are present, this TF "signal" is modified to

$$A(t) = \sum_l A_l(0)G_{xx}^l(t)\cos(\omega_l t + \phi_l) \ .$$

In this work a TF magnitude $H_0 \cong 220$ Oe was chosen so that H_0 would be high compared to typical dipolar fields and yet not high enough to deflect appreciably the μ^+ beam in the apparatus.

The FμF configuration for the diamagnetic muon fraction f_d was deduced mainly from the orientation dependence of the TF-μSR spectra, as shown in Figs. 1 and 2 for the case of NaF at 100 K. Two features are readily apparent in the data of Fig. 1: First, the asymmetry (amplitude) of the precession signal is reduced by a factor $f_d = 1 - f_{\text{Mu}}$ [relative to the value 0.322(2) measured in Al] due to the fraction f_{Mu} of the muons that initially thermalize as Mu atoms, whose low-field magnetogyric ratio $\gamma_{\text{Mu}} \cong 103\gamma_\mu$ causes them to precess at a much higher frequency and to be depolarized by their interactions with nuclear spins in $< 10^{-8}$ s.[2,5] Second, and of primary interest here, the precession signal displays a clear beat pattern. Similar splittings of the μ^+ precession frequency have been reported before[14] for TF-μSR measurements in gypsum (CaSO$_4\cdot$2H$_2$O), where the μ^+ replaces a proton in one of the waters of hydration; however, in that case the beat pattern was just barely observable. In the FμF system the splitting is well resolved, as revealed clearly in the Fourier-transform (FT) frequency spectra of Fig. 2. When the μ^+ spin **S** interacts with the spins **I**^{l} of lattice nuclei in the presence of a comparatively high external field **H**$_0$ (neglecting quadrupolar effects), only secular terms (proportional to $S_z I_z^l$) need to be considered in the spin Hamiltonian.[15] Theoretical FT spectra were calculated in this limit for the μ^+ located in a tetrahedral interstitial position and for the μ^+ bonded to anion nuclei along the $\langle 110 \rangle$, $\langle 111 \rangle$, and $\langle 100 \rangle$ directions. The FμF assumption (i.e., bonding along the $\langle 110 \rangle$ directions to two anions) was the only case in qualitative agreement with the observed frequency spectra; the line spectra predicted for a dipolar in-
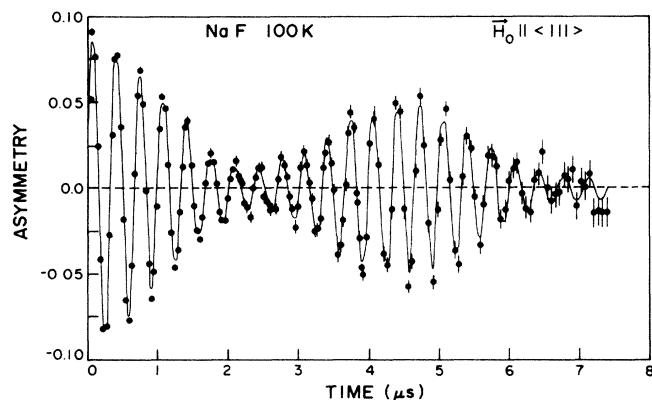
teraction frequency $\nu_d = 0.220$ MHz (defined below) are shown with the data in Fig. 2. For the case of $H_0 \parallel \langle 111 \rangle$, where the splitting is both predicted and observed to be the largest, a three-frequency χ^2 minimization fit was made to the $A(t)$ spectrum. This fit yielded a central frequency of 2.9980(7) MHz with lower and upper sideband splittings of 0.1983(15) MHz and 0.2204(15) MHz, respectively. The simple FμF model predicts both sidebands split equally by the dipolar interaction frequency $\nu_d = \omega_d/2\pi$, where

$$\hbar\omega_d = \gamma_\mu\gamma_F/r^3 \ , \tag{1}$$

and r is the μ^+-^{19}F distance, which is thus determined to have a value $r = 1.17(6)$ Å if we use the average of the two splittings. The 10% asymmetry in the splitting can be accounted for by imperfect alignment between **H**$_0$ and the $\langle 111 \rangle$ axis. Inasmuch as the nominal F$^-$ ionic radius is about 1.16 Å, the above value of r implies that the two F$^-$ ions can be visualized as hard spheres just touching, with the μ^+ located at the point of contact. This is the image of hydrogen bonding of two F$^-$ ions by an H$^+$ ion, or in this case by its light analogue, μ^+. For comparison, r is nearly
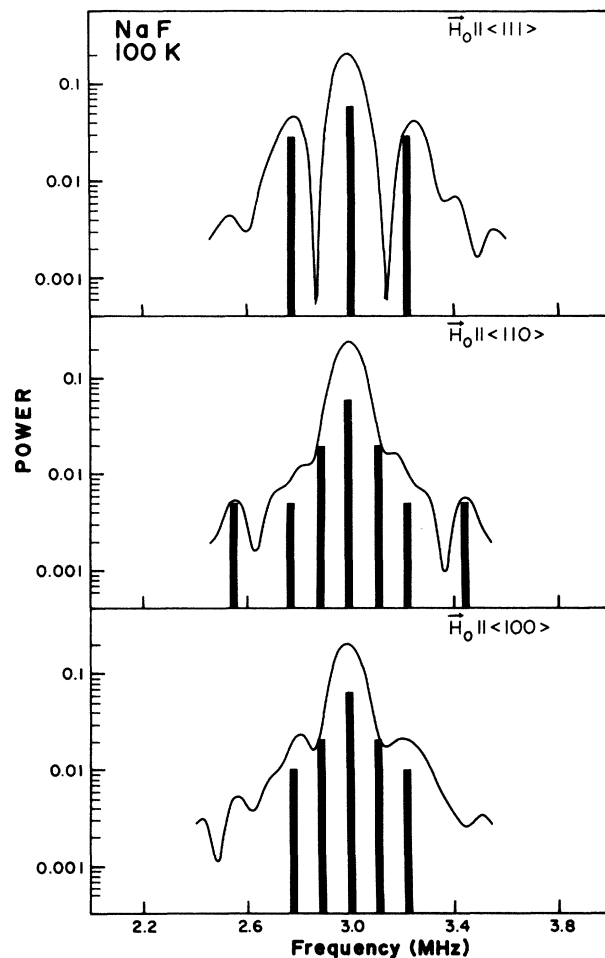
FIG. 2. Fourier-transform frequency spectra of the TF-μSR signals in NaF at 100 K with the indicated crystal axes aligned parallel to an applied magnetic field $H_0 \cong 220$ Oe. The bar diagrams are predicted line spectra for the collinear FμF configuration along the $\langle 110 \rangle$ direction, through use of a dipolar interaction frequency $\nu_d = 0.220$ MHz.

FIG. 1. TF-μSR precession signals $A(t)$ in NaF at 100 K with $H_0 \cong 220$ Oe along the crystalline $\langle 111 \rangle$ axis. The solid line is the minimum-χ^2 fit discussed in the text.
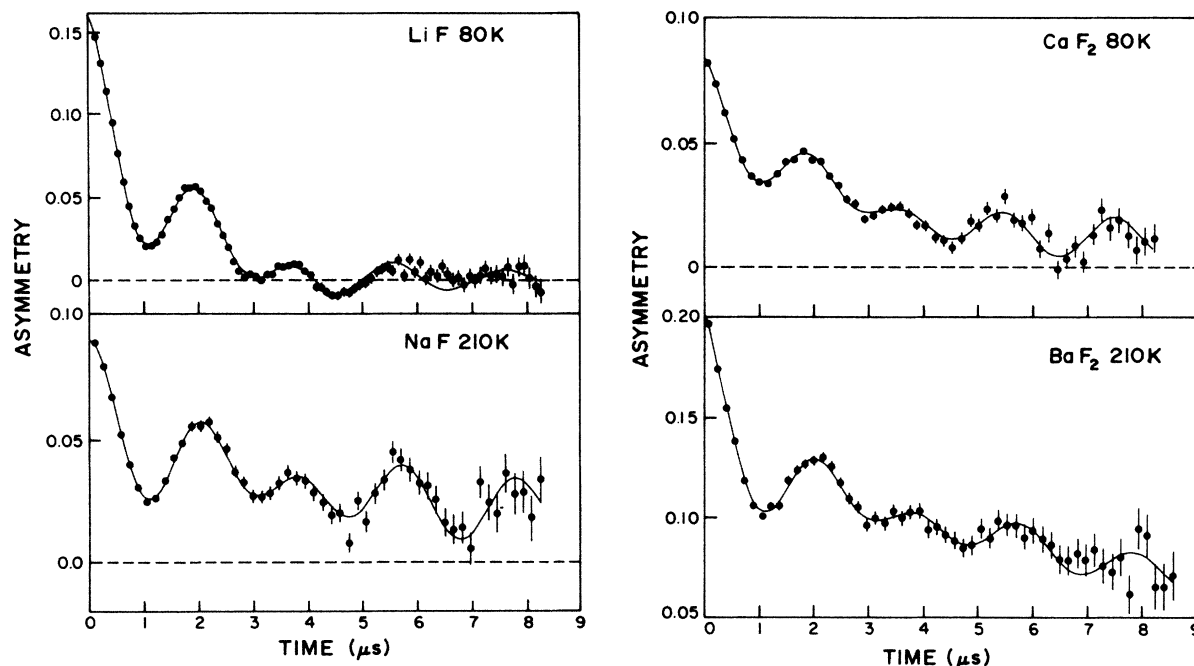
FIG. 3. ZF-μSR asymmety spectra $A(t)$ for several metal fluoride crystals at the indicated temperatures, with the crystalline $\langle 100 \rangle$ axis parallel to the initial muon polarization. The solid line in each case is a fit to Eqs. (2) and (3); the parameters extracted from the fits are listed in Table I.

equal to the length ($\simeq 1.14$ Å) of the H^+—F^- bond in $NaHF_2$, widely regarded as a classic example of hydrogen bonding.[16]

This "hydrogen-bonded FμF" model is further supported by the ZF-μSR data, representative samples of which are displayed in Fig. 3 along with best fits to a model relaxation function,

$$A(t) = A_0\{(1-f_b)f_d\exp[-\Lambda(t)]G_{F\mu F}(t) + f_bG_b(t)\},$$
$$(2)$$

the results of which are listed in Table I. The FμF relaxation function $G_{F\mu F}(t)$ is defined below; the extra term represents a background signal from a fraction f_b of the muons that are evidently not associated with the FμF complex and may not have stopped in the sample at all (f_b is largest for samples that were sealed in thin plastic bags). The uncertain origin of f_b makes quantitative interpretation of f_d ambiguous; we note only that the diamagnetic fraction

TABLE I. Summary of parameters extracted from μSR time spectra by χ^2-minimization fits. The symbols ν_d and r are defined in Eq. (1) and F—F is the minimum separation of two ^{19}F nuclei in the unperturbed lattice. Note that the nominal diameter of the F^- ion is roughly 2.32 Å.

Crystal	T (K)	ν_d (μs^{-1})	$2r$ (Å)	F—F (Å)
NaF	15.0(2)	0.214(3)	2.38(1)	3.27
NaF	210(1)	0.217(2)	2.38(1)	3.27
LiF	89(2)	0.222(2)	2.36(2)	2.85
CaF$_2$	80(1)	0.226(2)	2.34(2)	2.73
BaF$_2$	211(2)	0.214(2)	2.37(2)	3.10

is small ($< 50\%$) in every case. As a first approximation, $G_{F\mu F}(t)$ was calculated from first principles in a three-spin model assuming a static collinear geometry with μ^+ at the center of the line joining two ^{19}F nuclei (quantization axis for the ZF problem) and considering only the μ^+-^{19}F dipole-dipole interactions. Averaging over equivalent directions in the cubic lattice, one obtains

$$G_{F\mu F}(t) = \frac{1}{6}\left\{3 + \cos(\sqrt{3}\omega_d t) + \left(1 - \frac{1}{\sqrt{3}}\right)\cos\left[\left(\frac{3-\sqrt{3}}{2}\right)\omega_d t\right]\right.$$
$$\left. + \left(1 + \frac{1}{\sqrt{3}}\right)\cos\left[\left(\frac{3+\sqrt{3}}{2}\right)\omega_d t\right]\right\}. \qquad (3)$$

The FμF relaxation envelope and the nondescript relaxation function $G_b(t)$ of the background signal were both treated empirically by use of a generalized exponential, $\exp[-\Lambda(t)]$, with $\Lambda(t) = (\lambda t)^\beta$. Values $\beta = 1$ and $\beta = 2$ of the phenomenological shape parameter β correspond, respectively, to the usual exponential and Gaussian cases. For LiF and NaF a value of $\beta \simeq 1.5$ gave the best fits, in qualitative agreement with the expectation that the relaxation in these cases is due to other nearby nuclear moments.[17] For CaF$_2$ and BaF$_2$, $\beta \simeq 0.5$; values of $\beta < 1$ indicate the presence of fast-relaxing components in the μSR signal. One may speculate that such components are due to the products of a heretofore undetected reaction pathway involving muonium.

The muon-fluorine bond lengths deduced from Eq. (1) by use of the ZF data are listed in Table I. For NaF the ZF result is consistent with the value of r obtained from the averaged TF data. With striking consistency, the ^{19}F nuclei have been "pulled in" by the μ^+ to a separation roughly

equal to twice the nominal F^- ionic radius of 1.16 Å, which in every case is considerably less than the rigid-lattice F-F separation.

The $F\mu F$ model of Eq. (3) describes the main features of the data well, but subtle effects such as the overall relaxation envelope are not correctly described by our empirical treatment. A more rigorous theory including the effects of cation nuclear moments, direct fluorine-fluorine dipolar coupling, cation displacements, quadrupolar interactions of cation spins with electric field gradients, and muon zero-point motion will be presented in a later publication.[17] Comparisons of experimental data with a more exact theory should allow determination of many structural details of the $F\mu F$ center.

In summary, this work has revealed the existence of a stable diamagnetic state of the positive muon in a variety of metal fluoride crystals, in which the μ^+ forms a hydrogen bond between two F^- ions at an average distance of roughly the F^- ionic radius, thus producing a massive local distortion of the lattice. Such hydrogen-bonded complexes are likely to be a ubiquitous feature of μ^+ (or H^+) behavior in

all metal fluoride crystals, regardless of crystal structure, and possibly in many other ionic solids as well. The $F\mu F$ complex is vividly evident for the case of F^- anions because of the large ^{19}F moment, the low dimensionality of the $F\mu F$ spin system, and the lack of complications due to anion quadrupole moments. Because of this simplicity, the $F\mu F$ spin system and its characteristic ZF-μSR relaxation function may also serve as a prototype example for the fully quantum mechanical calculations[18] of ZF muon relaxation that have recently begun to supplant the classical approximations of Kubo and Toyabe[9] and Hayano *et al.*[10]

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