Muonium Analog of Hydrogen Passivation: Observation of the Mu^+-Zn^- Reaction in GaAs

K. H. Chow,[1] B. Hitti,[2] R. F. Kiefl,[2,3] R. L. Lichti,[4] and T. L. Estle[5]

[1]*Department of Physics, University of Alberta, Edmonton, Alberta, Canada T6G 2J1*
[2]*TRIUMF, 4004 Wesbrook Mall, Vancouver, Canada V6T 2A3*
[3]*Canadian Institute for Advanced Research, University of British Columbia, Vancouver, Canada V6T 1Z1*
[4]*Department of Physics, Texas Tech University, Lubbock, Texas 79409-1051*
[5]*Department of Physics and Astronomy, Rice University, Houston, Texas 77251-1892*

(Received 12 March 2001; published 1 November 2001)

We report direct detection of the formation and subsequent breakup of a complex containing positively charged muonium (Mu^+) and a substitutional Zn_{Ga} acceptor in heavily doped p-type GaAs:Zn. Mu^+ diffuses above 200 K with a hop rate $\nu = \nu_0 e^{-E_\nu/k_B T}$ where $\nu_0 = (7.7 \pm 2.0) \times 10^8$ s^{-1} and $E_\nu =$ 0.15(4) eV. Above 350 K, it forms the complex with a trapping radius of 500 ± 200 Å. The Mu-Zn complex breaks up above 550 K with a dissociation energy of 0.88(7) eV and prefactor of $(5 \pm 4) \times 10^{12}$ s^{-1}. Above 750 K, the cyclic reaction $Mu^+ \leftrightarrow Mu^0$ takes place.

DOI: 10.1103/PhysRevLett.87.216403 PACS numbers: 71.55.Eq, 66.30.Jt, 76.75.+i

Hydrogen (H) is a very reactive and mobile impurity in semiconductors that quickly forms complexes with and passivates other defects and dopants [1], resulting in removal of electrical activity as well as dramatic modifications of the optical properties of the host. In GaAs, all the donors Si, Ge, Sn, S, Se, and Te and the acceptors Be, Mg, Cd, Zn, and C are passivated by hydrogen [2]. The passivation of both dopant types is possible because H is an amphoteric impurity that changes its charge state to act as a compensating defect in heavily doped semiconductors—in other words, H^+ is the equilibrium state in p-type materials while H^- is stable in n-type samples. Since H is oppositely charged compared to the ionized (majority) dopants, Coulomb attraction leads, with great efficiency, to the passivation reaction. This high reactivity means that most of the techniques used to investigate H in semiconductors are unable to probe important aspects of this problem, namely (i) *isolated* H before the reaction, and (ii) the formation and dissociation of the complex *as it happens.* Most of the microscopic structural information on H-dopant complexes in GaAs, all nonparamagnetic, comes indirectly from local vibrational mode spectroscopy. These studies indicate that in p-type GaAs at low temperatures, H sits near the center of the bond (BC site) formed by an acceptor and a host atom while at higher temperatures, and H undergoes local motion in the vicinity of the acceptor [3].

Muonium ($Mu^0 = \mu^+ e^-$) is a light pseudoisotope of hydrogen that also acts as an amphoteric impurity in semiconductors. It is now well recognized that studies of the three charge states $(+, 0, -)$ of Mu are the main, albeit indirect, source of experimental information on *isolated* hydrogen [4,5]. In sharp contrast, although suggestions of the muonium analog of the hydrogen passivation reactions with intentional dopants exist, at present no clear signature of a complex is available in any semiconductor. This not only implies that our knowledge of the fundamental aspects of Mu interactions in semiconductors is incomplete, but also means that muonium studies have not provided any detailed microscopic information regarding the analogous H-dopant passivation reactions in semiconductors. These difficulties are due to the short muon lifetime of 2.2 μs, a property essential for the highly successful studies of muonium in its isolated form, but is very inconvenient for passivation studies because the time scale ($\approx$10 μs) in muonium experiments is too short compared to the time required for Mu to form a complex. Furthermore, even if muonium is mobile enough at any particular temperature to encounter a dopant and form a complex, the Mu-dopant complex must be stable on this time scale to allow for its observation/characterization.

In this Letter, we report on the rich dynamics of Mu^+ in heavily doped p-type GaAs:Zn from 5 to 1000 K. Our most interesting result is the detection of the formation of a muon-zinc complex. We believe that this is the first *direct* observation of a reaction between an isolated muonium or hydrogen center and an impurity in a semiconductor. In this study, we quantify the diffusivity of the precursor Mu^+ state, estimate the trapping radius of the zinc atom for the muon, and characterize the structure and stability of the muon-zinc complex.

The μSR (muon spin relaxation/rotation/resonance) experiments reported here were performed on either the M15 or M20B beam lines at TRIUMF where positive muons with a nominal momentum of 28 MeV/c and a spin polarization close to 100% are implanted into the samples. Three techniques, zero-field μSR, transverse-field μSR, and muon-level crossing resonance (μLCR), were used. These techniques are briefly described below as needed, with further details available in Ref. [4]. Our main results were obtained in three heavily doped p-type GaAs:Zn samples obtained from Crystal Specialties International. We label them as GaAs-A, GaAs-B, and GaAs-C, corresponding to Zn concentrations of $(4-5) \times 10^{18}$ cm^{-3}, $(0.8-1.1) \times 10^{19}$ cm^{-3}, and $(1.84-4.27) \times 10^{19}$ cm^{-3}, respectively.

 © 2001 The American Physical Society

In our heavily doped p-type GaAs:Zn samples, only the positive charge state of muonium (Mu^+) is observed. A very sensitive way of studying the kinetics of this diamagnetic center is to monitor the time evolution of the muon spin polarization $p(t)$ in zero applied magnetic field [6]. Figure 1 (inset) shows a typical spectrum. The data can be modeled with the "static Kubo Toyabe" (sKT) [7] function where $p(t) = \frac{1}{3} + \frac{2}{3}(1 - \Delta^2 t^2)\exp[-\frac{1}{2}\Delta^2 t^2]$. This is the functional form for a static Mu^+ center precessing in isotropic random Gaussian-distributed magnetic fields which in our samples are due to Ga and As nuclear dipoles ($I = 3/2$, 100% abundant). The parameter Δ, equal to $\gamma_\mu \langle B_\mu^2 \rangle^{1/2}$ where γ_μ is the muon's gyromagnetic ratio ($2\pi \times 135.54\ \mu s^{-1}\ T^{-1}$), measures the spread of these fields. The sKT function is strictly valid only for a *static* center. However, it models our experimental data well at *all* temperatures; hence we have used Δ over the full range as a phenomenological measure of the depolarization rate, which in turn depends on the strength of nuclear dipolar interactions and the dynamics.

The temperature dependence of Δ is shown in Fig. 1. Five distinct temperature regions can be clearly identified. Below 180 K (region I), Δ is independent of temperature and the concentration of Zn dopants, indicating that Mu^+ is *isolated* and *static* in this region. A small longitudinal field of $\approx$10 mT fully quenches the relaxation, confirming that it arises from weak nuclear dipolar fields. Our experiments, to be discussed in a future publication, confirm that isolated Mu^+ is located near the center of a Ga-As bond (BC site), consistent with theoretical calculations for Mu^+ or H^+ in GaAs [3,8]. At higher temperatures, in region II, Mu^+ *diffuses* through the crystal. Here Δ is reduced because the dipolar interaction is motionally averaged. Roughly speaking, the measured Δ is given by Δ_s^2/ν, where ν is the hop rate and Δ_s is the static value

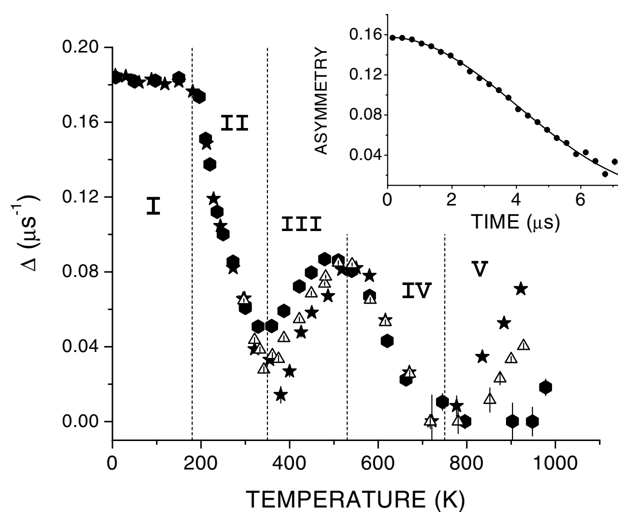

FIG. 1. Temperature dependence of the sKT relaxation rate Δ. The stars, open triangles, and closed hexagons correspond to GaAs-A, GaAs-B, and GaAs-C, respectively, The inset shows a typical zero-field spectrum (GaAs-A at 88 K). The solid line is a fit to the raw data using the sKT function.

in region I. More accurate values of ν can be obtained as indicated below. The physics occurring in regions III and IV is perhaps the most interesting. The "hump" structure is a clear signature [9] of the *trapping* of Mu^+ at an impurity (region III), followed by *detrapping* (region IV) as the temperature is increased. It is reasonable to expect the trapping center to be a Zn atom, the intentional dopant in our samples. This is confirmed by the observation that in region III, Δ scales monotonically with the Zn dopant concentration. Furthermore, as discussed below, the cross section for the reaction is as expected for trapping of Mu^+ at a negatively charged impurity, i.e., Zn^- acceptor. The Coulombic nature of the cross section also implies that Mu^+ is not reacting with positively charged or neutral intrinsic donors, even if they are created at concentrations comparable to Zn due to self-compensation of the Zn acceptors. Finally, in region V, there is a sharp increase in Δ which is strongly dependent on the Zn concentration. The line shape becomes more exponential, although it can still be adequately described by the sKT function, and is not quenched by a small magnetic field. This implies that the relaxation is due to charge state fluctuations between Mu^+ and Mu^0 [4,6,10] rather than to nuclear dipoles. Having identified the processes associated with the various regions, we elaborate first on the dynamics associated with Mu^+, then discuss the Mu^+-Zn^- complex.

In region II, Mu^+ is diffusing within the GaAs host lattice. The "dynamic Kubo Toyabe" (dKT) function $P_{ZF}(t) = p_s(t)e^{-\nu t} + \nu \int_0^t p_s(\tau)e^{-\nu\tau}P_{ZF}(t-\tau)\,d\tau$, which can be solved numerically for the polarization $P_{ZF}(t)$, is expected to model the zero-field data [7]. Here $p_s(t)$ is the sKT function describing the isolated static Mu^+ state and ν is the hop rate of Mu^+. First, the sKT function is used to fit the data in region I where the isolated Mu^+ center is static, giving $\Delta = 0.183(1)\ \mu s^{-1}$. The value of Δ is then fixed and the data in region II are fitted by the dKT equation to obtain ν. The temperature dependence of ν is plotted in Fig. 2(a). The diffusion of Mu^+ is well described by an Arrhenius law $\nu(T) = \nu_0 e^{-E_\nu/k_B T}$ where $\nu_0 = (7.7 \pm 2.0) \times 10^8\ s^{-1}$ and the energy barrier for diffusion is $E_\nu = 0.15(4)$ eV. The similarity between these values and the prefactors and energies obtained for many reorientating hydrogen and deuterium-acceptor complexes in Si and GaAs (see Fig. 2 in Ref. [11]) suggest that the diffusion of Mu^+ through the lattice (from one BC site to a neighboring one) may be due to an analogous "thermally activated tunneling" [12] mechanism.

It is also interesting to contrast the motion of isolated Mu^+ with that observed for Mu^- in heavily doped n-type GaAs:Si [6] and Mu_T^0 in semi-insulating GaAs [13]. Mu^+ starts moving at lower temperatures compared to Mu^-, and has a significantly lower activation energy for diffusion ($\sim$0.73 eV for Mu^-). *Ab initio* molecular dynamics calculations [8] predict that the diffusion barrier should indeed be lower for Mu^+ (H^+). Our experimental value compares well with that of H^+ in SI-GaAs of $0.2 \pm >0.1$ eV obtained from perturbed angular correlation experiments

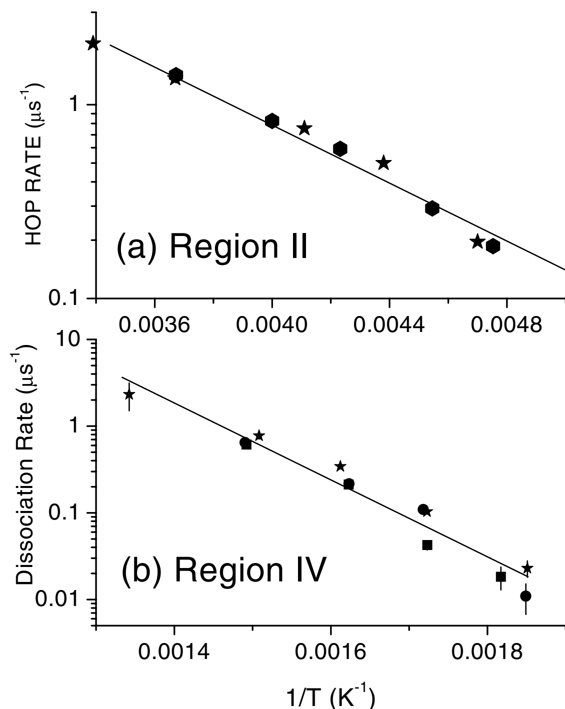

FIG. 2. The temperature dependence of the (a) hop rate and (b) dissociation rate of Mu^+ in our GaAs samples. The symbols have the same meaning as in Fig. 1.

[14]. The experimental hop rate of Mu^- is 9 orders of magnitude smaller than for Mu^0 [6] at room temperature. Although not as dramatic, the measured diffusivity of Mu^+ at room temperature is still $\approx 10^3 - 10^4$ times lower than for Mu^0. Translating to hydrogen, we propose that, like in n-type GaAs, at high temperatures where charge cycling takes place, the diffusion of hydrogen in p-type GaAs is likely governed by the fraction of time hydrogen spends as a neutral center.

Our main goal in region III is to estimate the trap radius r_R for the reaction between Mu^+ and a Zn dopant. The expression [9]

$$r_R = \frac{2\pi}{3} \frac{c_R x^2 \nu}{\nu_R} \tag{1}$$

relates the trapping radius r_R to the trapping rate ν_R, the concentration of traps c_R, the isolated Mu^+ hop rate ν, and the mean hop distance x. We assume that c_R is the zinc concentration, ν is the Arrhenius expression obtained above and $x = a/\sqrt{8}$, appropriate for adjacent BC positions in a semiconductor with a lattice constant a. This leaves only ν_R unknown. An extrapolation of ν to the temperatures of region III confirms that the diffusion of Mu^+ is rapid enough that $P_{\mathrm{ZF}}(t) \approx 1$. In this limit, the dynamics governing this reaction can be solved within a strong-collision [4,15] approach to give the polarization function $R_z(t) = e^{-\nu_R t} + \nu_R \int_0^t e^{-\nu_R \tau} q(t - \tau)\, d\tau$ where $q(t)$ describes the spin polarization of the muon-zinc complex. Here $q(t)$ is the sKT expression with $\Delta_R = 0.0865(2)\ \mu\mathrm{s}^{-1}$, a very good fit to the data at the trapping peak. Hence, ν_R can be obtained by fitting the data of region III to $R_z(t)$. Subsequent application of Eq. (1) leads to an estimate of $r_R \approx 500 \pm 200$ Å. The large trapping radius is appropriate for a Coulomb capture process, as expected if the positively charged Mu^+ center traps at a negatively charged Zn^- acceptor.

In region IV, there is information on the dissociation of the Mu-Zn complex. An appropriate depolarization function $D_{\mathrm{ZF}}(t)$ in this region can also be derived using the strong collision approach: $D_{\mathrm{ZF}}(t) = q(t)e^{-\nu_D t} + \nu_D \int_0^t q(\tau) e^{-\nu_D \tau}\, d\tau$ where ν_D is the dissociation rate of the complex and the static spin polarization of the complex $q(t)$ is as described above. The temperature dependence of ν_D is shown in Fig. 2(b). A fit to the Arrhenius expression $\nu_D = \nu_{D0} e^{-E_D/k_B T}$ gives $\nu_{D0} = (5 \pm 4) \times 10^{12}\ \mathrm{s}^{-1}$ and $E_D = 0.88(7)$ eV. The prefactor is typical of phonon frequencies and the dissociation energy for Mu-Zn_{Ga} is lower but comparable to those for hydrogen in other acceptor-related complexes, which range from ≈ 1.15 to 1.45 eV [16].

In region V, the cyclic reaction $Mu^+ \leftrightarrow Mu^0$ is occurring. Such charge state fluctuations are commonly observed at high temperatures for muonium in semiconductors [4,6,10]. In this region, Mu^+ can capture a free minority electron and convert to Mu^0, but rapidly becomes Mu^+ again by either ionizing or capturing a hole. Consequently, the depolarization rate is proportional to the electron capture rate, which in turn scales with the free minority electron concentration. Hence, the observed Δ is largest in the "least" p-type GaAs:Zn sample.

Finally, we elaborate on the structure of the muon-zinc complex. The techniques used for this purpose are Hartmann depolarization and μLCR, which are described in more detail in Refs. [17,18]. Figure 3(a) shows the magnetic field dependence of σ for the isolated state ($T = 50$ K) and the muon-zinc complex ($T = 490$ K) in GaAs-C where the applied field $\mathbf{B} \parallel \langle 100 \rangle$. The parameter σ characterizes the Gaussian relaxation of the signal precessing at the Larmor frequency when $\mathbf{B}$ is applied transverse (TF) to the initial muon spin. It depends on both the dipolar interaction and the muon-induced quadrupolar interaction Q with the Ga and As host atoms [19]. The prominent drops in σ at both temperatures for this field orientation implies that θ, the angle between $\mathbf{B}$ and the muon-nucleus direction, is close to 54.7°. Hence, the muon and nucleus dominating the dipolar interaction lie on the same $\langle 111 \rangle$ axis, as would be expected for Mu^+ located at a BC site. The crossover field B_{cr} between the low field and high field values of σ is a measure of the quadrupole interaction, i.e., $Q \approx \gamma_N B_{cr}$. Our data in Fig. 3(a) demonstrate that Q(complex) is at least an order of magnitude smaller than Q(isolated). This estimate defines a search region for our μLCR experiments, with results for the complex shown in Fig. 3(b). A doublet signal is observed with no other resonances visible up to ≈ 40 mT. Resonances occur at magnetic fields where cross relaxation between the muon and neighboring nuclear spins take place as determined by Q and θ. The

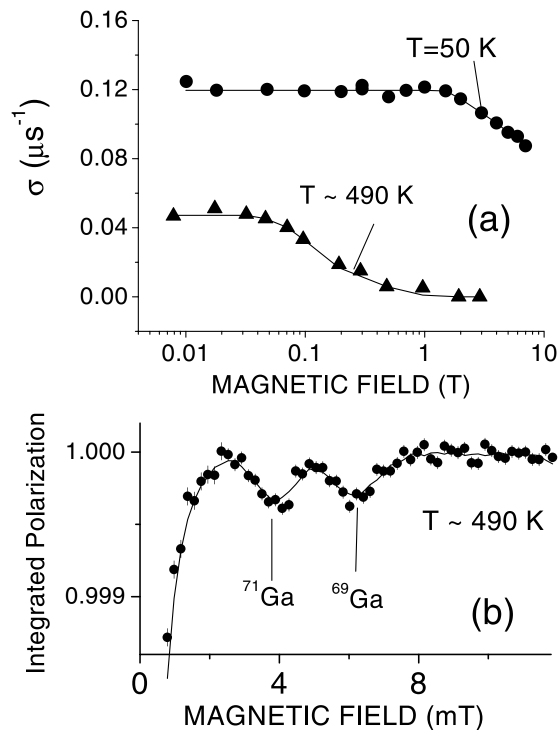

FIG. 3. (a) Transverse-field relaxation σ as a function of applied magnetic field for the isolated Mu^+ and the Mu-Zn complex. (b) μLCR spectrum of the Mu-Zn complex. The solid lines in both are guides to the eye.

ratio of the positions of the two resonances (1.60 ± 0.02) is very close to the ratio of the ^{69}Ga and ^{71}Ga quadrupole moments (1.589) and the relative intensities are as expected from natural abundances and dipole moments, providing strong evidence that the doublet signal is due to a neighboring Ga nucleus. This observation, as well as the dramatic difference between Q(isolated) and Q(complex), is intriguing since many theoretical calculations place the muon or hydrogen near the center of a Zn_{Ga}-As bond [3,8] when it is complexed. Since Zn-H(Mu) bonds are much weaker than As-H, the Mu^+ is strongly attached to the As in the static complex and one should observe a resonance due to the nearby ^{75}As nucleus. Our data imply that Mu^+ remains trapped near the Zn at 500 K; however, it could be undergoing rapid local motion around the As and only occasionally visiting the Zn-As bond. Regardless of whether such motion is of classical or quantum origin, it would average out interactions with the As and leave the next-neighbor Ga nuclei observable, but with a significantly reduced mean quadrupolar coupling compared to the BC site of a static isolated Mu^+. Interestingly, low-temperature anelastic relaxation in GaAs:Zn [11] implies extremely fast local tunneling of D different from that involving the four BC sites around the Zn dopant as is typically observed for other H-acceptor complexes.

In conclusion, we have directly observed the Coulombically governed reaction between an isolated Mu^+ and a Zn^- dopant in heavily doped p-type GaAs:Zn. We have characterized the motion of the isolated Mu^+ state and the formation and dissociation of the Mu-Zn complex, and have investigated the (high-temperature) structure of the complex. Our results for diffusion of Mu^+ in GaAs are comparable to the sparse data available on H^+. The dissociation energy of the Mu-Zn complex is slightly smaller than that of similar H-acceptor complexes in GaAs. Surprisingly, our data suggest a structure for the Mu-Zn complex at 500 K that is different from either the commonly accepted static ground state configuration of an H-acceptor pair or its dynamic counterpart. It is unclear if this result implies a different structure for H-Zn compared to other H-acceptor complexes, represents a general excited state of such complexes, or is a consequence of some fundamental difference between H and Mu. Hence, these intriguing results strongly suggest the need for additional theoretical modeling of alternative structures for acceptor-related H/Mu complexes that also incorporates the dynamical variations (and other differences) between H and Mu within such complexes.

This work is funded by NSERC of Canada (K. H. C., B. H., R. F. K., TRIUMF), the Robert A. Welch Foundation (R. L. L. [D-1321]), and the National Science Foundation (R. L. L. [DMR-0102862]).

[1] For an overview see S. J. Pearton, J. W. Corbett, and M. Stavola, *Hydrogen in Crystalline Semiconductors* (Springer, Berlin, 1992); S. M. Myers *et al.,* Rev. Mod. Phys. **64**, 559 (1992).
[2] R. Rahbi *et al.,* J. Appl. Phys. **73**, 1723 (1993).
[3] A. A. Bonapasta *et al.,* Phys. Rev. B **57**, 12 923 (1998), and references therein.
[4] K. H. Chow, B. Hitti, and R. F. Kiefl, in *Identification of Defects in Semiconductors,* edited by M. Stavola (Academic Press, New York, 1998), p. 137.
[5] For review of Mu in semiconductors see B. D. Patterson, Rev. Mod. Phys. **60**, 69 (1988); R. F. Kiefl and T. L. Estle, in *Hydrogen in Semiconductors,* edited by J. Pankove and N. M. Johnson (Academic, New York, 1990), p. 547.
[6] K. H. Chow *et al.,* Phys. Rev. Lett. **76**, 3790 (1996).
[7] R. S. Hayano *et al.,* Phys. Rev. B **20**, 850 (1979).
[8] C. Wang and Q.-M. Zhang, Phys. Rev. B **59**, 4864 (1999).
[9] O. Hartmann *et al.,* Phys. Rev. B **37**, 4425 (1988).
[10] K. H. Chow *et al.,* Phys. Rev. B **50**, 8918 (1994).
[11] G. Cannelli *et al.,* Solid State Commun. **98**, 873 (1996).
[12] C. P. Flynn and A. M. Stoneham, Phys. Rev. B **1**, 3966 (1970).
[13] R. Kadono *et al.,* Hyperfine Interact. **64**, 635 (1990).
[14] A. Burchard *et al.,* Mater. Res. Soc. Symp. Proc. **513**, 171 (1998).
[15] S. R. Kreitzman *et al.,* Phys. Rev. B **51**, 13 117 (1995).
[16] S. J. Pearton, Mater. Sci. Forum **148-149**, 393 (1994).
[17] O. Hartmann, Phys. Rev. Lett. **39**, 832 (1977).
[18] Successful application of these techniques is illustrated for Mu^- in n-type GaAs in K. H. Chow *et al.,* Phys. Rev. B **51**, 14 762 (1995), and Ref. [4].
[19] Only 4.1% of the zinc atoms (^{67}Zn, $I = 5/2$) have nonzero magnetic moment.