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Landau diamagnetism of a weakly bound muonium atom

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Abstract

The ionization with temperature of weakly bound muonium atoms in undoped CdS has been studied using the technique of muon spin relaxation in a transverse magnetic field of 10 mT. For this atom the Coulomb binding energy between the muon and the electron is sufficiently small that the Landau diamagnetic term determines the magnetic behavior of the system: due to the diamagnetic interaction the muon precession in a transverse magnetic field exhibits a frequency shift of approximately 0.5% around the ionization temperature.

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The problem of weakly bound atoms in a magnetic field is connected with diamagnetism and, at its simplest, concerns the dynamics of the electron when submitted to the joint actions of Coulomb and magnetic fields of comparable strength. The fundamental nature of the problem makes it archetypal to a wide class of phenomena in various branches of physics ranging from solid state physics to astrophysics. It has applications in solid state physics of excitonic systems [1] and two-dimensional electron layers [2], in heavy ion collisions [3] and laser physics [4], in plasma physics [5] and astrophysics of pulsars and white dwarfs [6].

The possible importance of diamagnetism for weakly bound electronic systems was first theoretically established by Landau [7]. Experimental evidence of the diamagnetic shift in atomic spectra was found in Na atoms [8] and the existence of individual diamagnetic levels was observed for highly excited Ba atoms [9]. In the latter experiment the authors demonstrated the existence close to the ionization limit of a new structure (neither Coulombic nor Landau) of the atomic spectrum which is now known as the quasi-Landau or strong-field-mixing regime [2]. Further advances in the understanding of the physics of weakly bound or highly excited Rydberg [10,11] atoms in external fields has been stimulated by the results of numerous experiments using tunable lasers to excite atoms.

To date, however, the behaviour for comparable Coulomb and magnetic interactions remains an un-

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solved problem even for the hydrogen atom with the simplest form of Hamiltonian [10]:

$$H=\frac{p^2}{2}-\frac{1}{r}+\frac{\vec{L}\vec{B}}{2}+\frac{1}{8}\left(x^2+y^2\right)B^2; \tag{1}$$

here the third and last terms represent the Zeeman and diamagnetic interactions, respectively; the external magnetic field B is given in atomic units (2.35×10^5 T). Difficulties arise because Hamiltonian (1) is nonseparable, the Coulomb symmetry being broken by the action of an external field of different symmetry but similar strength. In the two perturbation limits when either Coulomb or magnetic interaction is dominant, the eigenvalues can easily be found and yield the Rydberg and Landau spectra, respectively. In the intermediate regime, however, where both interactions are comparable the perturbation treatment is not appropriate. Since the full Hamiltonian is not separable, determination of the eigenvalues becomes extremely difficult; it is this region of the spectrum that is of particular interest, since it is here that the overall structure changes from Rydberg-like to Landau-like as the atom approaches the ionization limit. Recent experiments studying highly excited hydrogen atoms [12] convincingly demonstrated the decisive role of atomic diamagnetism in the quasi-Landau regime. In this Letter we present experimental evidence for a diamagnetic shift at the ionization threshold of the muonium ($\mathrm{Mu} \equiv \mu^+e^-$) atom, an isotope of hydrogen with a positive muon (μ^+) as the nucleus.

Although the muon is an order of magnitude lighter than the proton ($m_\mu \approx m_p/9$), it is so much heavier than the electron that the reduced masses are the same to within a fraction of a percent in the Mu and H atoms [13]. Consequently, muonium has essentially the same ionization potential (13.54 eV) and Bohr radius in its vacuum state as protium. For this reason muonium may properly be considered a light hydrogen isotope; as such, Mu is expected to exhibit electronic states analogous to those of H. This image has inspired and underpinned extensive studies through the nuclear-detected technique of muon spin rotation/relaxation (μ^+SR) [13] which have greatly extended our understanding of the states and dynamics of interstitial hydrogen and, in certain cases, completely upset established views. Thus in semiconductors, muonium states were discovered for which the site and local electronic structure differed considerably from the expected trapped-atom state. We refer in particular to the so-called anomalous muonium state in Si, GaAs, etc., now understood to have a somewhat extended electron distribution associated with a bond-center site [14]. These states were quite unanticipated but have substantially shaped current understanding of interstitial hydrogen and its deep-level electrical activity. Most recently, μ^+SR studies have played their part in establishing the existence also of shallow donor hydrogen states, in II–VI compound semiconductors such as CdS [15] and ZnO [16,17].

In μ^+SR experiments one accumulates the necessary statistics into a time spectrum by following the spin polarization of 4 MeV positive muons stopped in the sample. Each incoming muon leaves behind an ionization track of excess electrons and ions liberated during the μ^+ thermalization process. Experiments in insulating (liquid helium [18], liquid and solid nitrogen [19,20], liquid [21] and solid neon and argon [22]) and, more recently, in semiconducting (Si [23] and GaAs [24]) media have shown that the spatial distribution of the ionization track products is highly anisotropic with respect to the final position of the muon: the μ^+ thermalizes well downstream from its last ionization event. Some of the excess electrons generated in the end of the μ^+ track turn out to be mobile enough to reach the thermalized muon and form the hydrogen-like muonium atom.

It has been customary to consider muonium dynamics in matter in terms of a relatively small number of sites and configurations (in tetrahedral semiconductors the cage-centered and bond-centered states)—all in their lowest or ground electronic states. Their ionic or ionized counterparts are included in descriptions of the interplay of site and charge state but without explicit details of intermediate states, whether vibrationally or electronically excited. For these electronic ground states, the diamagnetic term in Eq. (1) is negligible and muonium spin dynamics can adequately be described by the well-known Breit–Rabi Hamiltonian [13] with the limiting regimes of Zeeman and Paschen–Bach coming from the term proportional to B. However, the phenomenon of delayed muonium formation described above inevitably implies that as the electron approaches the muon it may be captured initially into a highly excited muonium atom with macroscopic-sized orbits, viz. a weakly bound metastable precursor of the ground state. Such Rydberg states would be susceptible to ionization either with temperature or with a sufficient electric field. It has long been known that Mu centers in semiconductors are ionized above several hundred Kelvin [14]; more recently, experiments in Si [23] and GaAs [24] demonstrate ionization in applied electric fields. In the III–V compound GaAs [24], the results suggest that bond-centered muonium, $\mathrm{Mu_{BC}}$, has a weakly bound precursor state (analogous to excitonic states in semiconductors [25]) which can be ionized in an electric field, impeding conversion to the ground state. In the wider-gap II–VI semiconductor CdS, recent experiments have revealed a novel muonium state, namely a long-lived shallow-level center with a binding energy of 18 meV and a characteristic Bohr radius of 1.4 nm [15] (by comparison, for the shallow donor precursor in GaAs the suggested values are 7 meV and 8.3 nm, respectively [24]).

For these weakly bound atoms at the ionization threshold, the diamagnetic term in Eq. (1) scales as a^2B^2 (a is the size of the electronic orbit) and can no longer be ignored. In this Letter we present experimental evidence that the diamagnetic interaction does play an important role in the dynamics of the shallow-level Mu state.

The experiments were performed on the EMU beam line of the ISIS pulsed muon facility at the Rutherford Appleton Laboratory. We used an undoped single crystal of CdS sample, as studied in Ref. [15] and known to exhibit the shallow-level Mu center. Positive muons of 28 MeV/c momentum and 100% spin polarization were stopped in the sample and μ^+SR time spectra were recorded at various different temperatures. The transverse field technique [13] was used at an applied magnetic field $B = 0.01$ T. The time differential μ^+SR technique relies on positrons from the muon decay being emitted preferentially along the direction of the muon polarization. The resultant muon decay asymmetry directly reveals the amplitudes of the characteristic precession signals.

With the magnetic field applied perpendicular to the initial muon spin polarization two typical muon states—diamagnetic (usually the “bare” muon or molecular ion) and paramagnetic (usually a muonium atom)—can easily be distinguished by their respective Larmor frequencies: in weak (∼0.1 mT) transverse magnetic fields, those muons which form Mu precess at a characteristic triplet Larmor frequency $\nu_{\mathrm{Mu}} \approx -103\nu_\mu$, where $\nu_\mu = \gamma_\mu B$ is the Larmor frequency of a muon in a diamagnetic environment and $\gamma_\mu = 135.5$ MHz/T is the muon gyromagnetic ratio (triplet muonium precess in the opposite sense to the μ^+, having essentially the electron’s magnetic moment, hence the negative sign). At higher magnetic fields, the muonium precession splits into two lines, their separation determined by the muon–electron hyperfine interaction $A_0 = 4463$ MHz. This discussion is restricted, however, to the case where muonium is unperturbed by interactions with the environment, i.e., vacuum state muonium.

In semiconductors, different muonium states typically exhibit hyperfine interactions that are reduced with respect to that for vacuum state muonium [14]: for isotropic muonium centers the hyperfine interaction is usually about half the vacuum value, for anisotropic Mu it is typically even smaller (though still significant). The remarkable feature of the Mu state observed in CdS [15] is that the hyperfine interaction A is extremely small, amounting to only about 10^{-4} of the vacuum value. For this state, even a modest magnetic field of 0.01 T sets up the high field limiting case ($A \ll \gamma_\mu B$) with muonium frequencies positioned symmetrically about the diamagnetic signal at $\nu_{\mathrm{Mu}} = \nu_\mu \pm A/2$ [13]. Fig. 1 presents the Fourier transform of the μ^+SR spectra measured in the CdS sample with magnetic field of 0.01 T applied perpendicular to the initial muon spin polarization and parallel to the ab plane of the crystal. At low temperatures ($T = 3.55$ K), the μ^+SR spectrum consists of several lines: the central line corresponding to the Larmor precession frequency of the bare muon and satellite lines positioned close to and symmetrically about the central one. A best fit to the data shows that the envelope of each satellite line consists of the superposition of more than one line. In the geometry of the present measurements, the Cd–S bond on the c-axis is at $\theta = 90°$ to the external field, two of the other bonds are at angles close to $\theta = 70°$ and the fourth at around $\theta = 20°$ to the external field. Most of the weight in the frequency spectrum (see Fig. 1) is related to muonium with its symmetry axis in the direction of the bonds at $\theta = 90°$ and $\theta = 70°$ and the external shoulders are related to muonium along the bond at lower angle. This frequency distribution and the measured values of the relative positions of the satellite lines are in complete agreement with the hyperfine parameters from Ref. [15], where the measurements with the applied

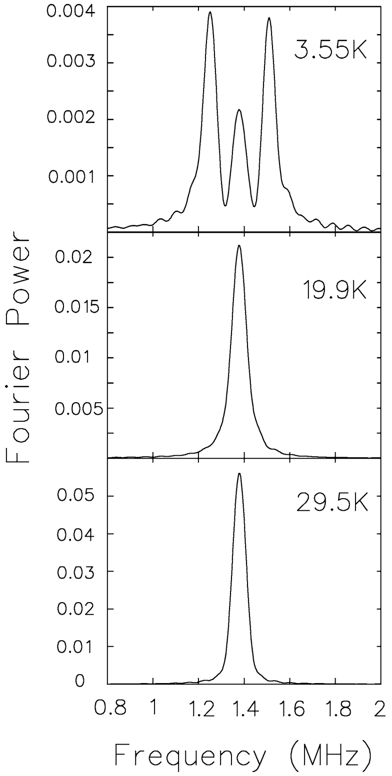

Fig. 1. Fourier transform of μ^+SR spectra in CdS in a transverse magnetic field of 0.01 T at several temperatures (3.55, 19.9 and 29.5 K).

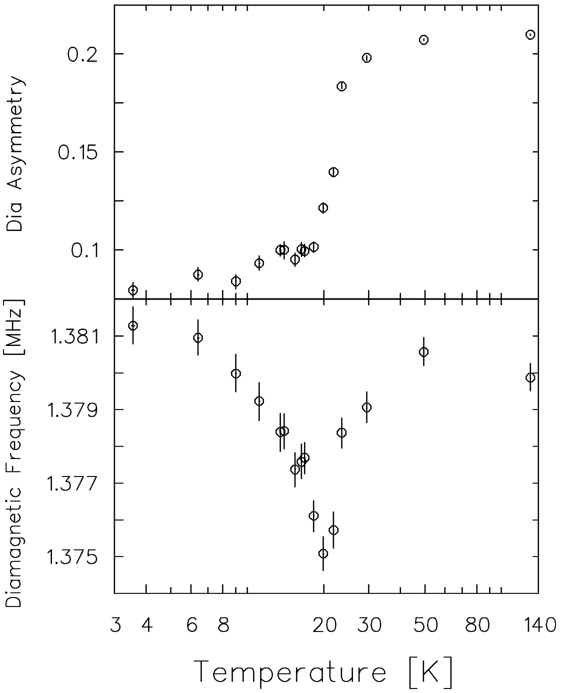

Fig. 2. Temperature dependencies of (a) the amplitude (asymmetry) of the central line and (b) precession frequency of the central spectral line in CdS in a transverse magnetic field of 0.01 T.

magnetic field along the c-axis allowed the authors to show that the noncentral lines represent muonium precession frequencies with a hyperfine interaction axially symmetric along the Cd–S bond direction; the lines representing $\theta = 0°$ and $\theta = 70°$ were well separated in those measurements. The isotropic part of the hyperfine interaction was determined to be 244 kHz, which is smaller than the hyperfine interaction for vacuum state muonium by factor of 1.8×10^4 [15]. From these measurements the binding energy and the effective Bohr radius for Mu center in CdS were estimated to be approximately 18 meV and $26a_0$, respectively [15] (compared to 13.5 eV and $a_0 = 0.05$ nm for the vacuum state Mu or H atoms). These findings imply that the Mu center observed in CdS is a weakly bound atom with macroscopic-sized electronic orbits.

As the temperature is increased, the intensity of the central line grows at the expense of the satellite muonium lines. At 19.9 K the μ^+SR spectrum shows a characteristic beating, implying that all the spectral lines are still present; at 29.5 K a single line at the muon frequency is dominant, with only a very small admixture of muonium signals. Fig. 2(a) presents the temperature dependence of the central line amplitude measured in transverse magnetic field 0.01 T. The full asymmetry in this experiment is 0.21. At low temperatures a diamagnetic asymmetry of approximately 0.05 is measured, signals from the muonium states making up the remainder. At about 20 K a sharp rise of the central line is observed that is in agreement with previous measurements [15]. Above about 50 K the diamagnetic signal accounts for the full asymmetry. These measurements imply that muonium center in CdS ionizes in a similar manner to Mu atoms in other semiconductors [14], although the ionization temperature in CdS is much lower than in other semiconductors. This provides further evidence that the Mu center in CdS is a weakly bound atom. For such an atom, at the ionization threshold one would expect a significant energy shift (and correspondent frequency shift) even in a modest magnetic field due to the diamagnetic interaction.

Fig. 2(b) shows the temperature dependence of the central spectral line frequency in the CdS sample measured in a transverse magnetic field of 0.01 T. At low temperatures, apart from the 1.381 MHz precession of the diamagnetic muon fraction (one quarter of the total signal), the remaining signal is seen at frequencies corresponding to the weakly bound muonium atom with a characteristic size of electron orbit of $a = 26a_0$. For such an atom, the diamagnetic frequency shift can be estimated as [26]

$$\Delta\nu = \frac{1}{h}\frac{e^2}{12m^*c^2}B^2a^2, \tag{2}$$

where h is the Plank's constant, e is the electron charge, c is the velocity of light and $m^* = 0.2m_0$ is the effective electron mass in CdS. This estimate gives $\Delta\nu \approx 4\times10^{-4}$ MHz which cannot be observed in our experiment as the shift is small with respect to the typical muonium line width. At high temperatures (above about 50 K), the muonium atom is no longer formed in CdS and the diamagnetic fraction accounts for the full muon signal precessing at the same frequency as at low temperature. Around 20 K, however, a significant frequency shift of the central line is observed amounting to approximately 6×10^{-3} MHz. At 0.5% of the Larmor frequency, this is far greater than could be attributed to a Knight shift or to ground-state diamagnetism of the sort responsible for chemical shifts in conventional NMR spectroscopy.

At this temperature the muonium amplitude is about half of the full signal. Using Eq. (2) the observed frequency shift can be attributed to a muonium atom with $a \sim 100a_0$. This value may be compared with the effective Bohr radius for the weakly bound precursor state in GaAs: $a \approx 160a_0$ [24]. (For a highly excited hydrogen atom electron orbits have been suggested to extend even over $a \sim 1000a_0$ [12].)

A possible scenario is that muonium is formed via electron transport from the muon's track, as seen in many insulators [18–22] and semiconductors [23,24]. As the electron approaches the muon they form a weakly bound paramagnetic muonium atom. The intermediate state of this atom having $a \sim 100a_0$ exhibits a frequency shift due to the diamagnetic interaction. This happens only at low temperatures, however, as the binding energy of this atom is small.

In conclusion, we have measured a significant shift in muon precession frequency at approximately the ionization temperature of the weakly bound muonium atom formed in CdS. This shift is attributed to the diamagnetic interaction in a macroscopic-sized electronic system. This interaction may be important in other insulators and semiconductors where muonium or hydrogen atoms are for some reason formed at extended length scales, e.g., via electron transport to a positive center. The importance of such atoms is that, being in electrically active shallow states, they may profoundly modify the electronic properties of the host.

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