Bound magnetic polarons in the 3d-electron ferromagnetic spinel semiconductor CdCr$_2$Se$_4$

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Abstract
Muon spin rotation/relaxation spectroscopy has been employed to study electron localization into a bound magnetic polaron around the positive muon in the 3d magnetic spinel semiconductor CdCr$_2$Se$_4$ at temperatures up to 300 K (far above the ferromagnetic transition at $T_c = 130$ K) in magnetic fields up to 7 T. Electron localization into a magnetic polaron occurs due to its strong exchange interaction with the magnetic 3d electrons of local Cr$^{3+}$ ions, which confines its wavefunction to within $R \approx 0.3$ nm, allowing significant overlap with both the nearest and the next nearest shells of Cr ions. Formation of such magnetic polarons may explain peculiar electronic and magnetic properties of magnetic semiconductors.

(Some figures in this article are in colour only in the electronic version)

The semiconductors currently in use as working media in electronics and information technology (Si, Ge, GaAs etc) are nonmagnetic; therefore the spin of the carriers has so far played a minor role in semiconductor devices. One way to enhance spin-related phenomena for semiconductor spintronics applications [1, 2] is to incorporate magnetic ions (typically Mn) into nonmagnetic semiconductors to realize dilute magnetic semiconductors (DMS) [3, 4]. The interplay between electric and magnetic properties in ferromagnetic (FM) Mn-doped III–V DMS has recently been demonstrated [5–7]. Combined with nonmagnetic semiconductors, these DMS may also serve as polarized spin injectors in spintronics devices [8, 9]. The FM in these p-type materials results from a long-range coupling between the Mn atoms mediated by holes generated by Mn substitution at the trivalent cation site [10].

Unfortunately, the ferromagnetism in Mn-doped III–V DMS is limited by the low concentration of magnetic ions. Molecular beam epitaxy can produce a non-equilibrium enhancement of the otherwise low solubility of transition metals in III–V hosts, but still allows incorporation of no more than about 7–8% of Mn atoms; above this critical concentration, Mn tends to cluster and phase separate [11]. Even at lower concentrations, spatial homogeneity may be affected by adding Mn [10] and nanoscale-range magnetic inhomogeneities may occur [12].

By contrast, intrinsic magnetic semiconductors (MS), such as the 4f Eu chalcogenides or 3d Cr spinels, exhibit spontaneous homogeneous ferromagnetic order without any doping. When doped, these MS show semiconducting behavior (both n- and p-type), which indicates strong mutual influences between electrical and magnetic properties [13, 14]. Successful demonstration of the epitaxial growth of EuO and CdCr$_2$Se$_4$ on technologically important semiconductors Si, GaN, GaAs and GaP [15–17] makes them very attractive working media for spintronics applications. These materials
offer several important advantages over DMS, such as higher magnetization, spatial homogeneity and wider ranges of conductivity tunable by doping. The longer spin lifetimes and spin-scattering lengths of electrons in Si, GaAs and GaN [17–19], as well as much higher electron mobilities compared with those of holes, make the ability to support n-type conductivity in MS especially attractive for semiconductor spintronics.

Since charge and spin transport for electrons in Si, GaAs, GaP and GaN is excellent, the effectiveness of prospective all-semiconductor spintronics devices is determined by the electron transport in doped magnetic semiconductors. These materials, however, can support states that lead to severe electron localization [14]. In fact, MS provide optimal conditions for the formation of a new type of quasiparticle—the magnetic polaron (MP)—in which conduction electron ‘autolocalization’ stabilizes an atomic-scale FM region well above \( T_c \) [20, 21, 14]. This electron localization in MS profoundly modifies their magnetic, electrical and optical properties. In particular, such MP determine most of the transport properties of magnetic semiconductors, leading to metal–insulator transitions with a remarkable resistivity change of up to 13 orders of magnitude (in doped EuO) and colossal magnetoresistance which suppresses resistivity by 3–4 orders of magnitude in magnetic fields of \( \sim 10 \) T [14]. Measurements of both resistivity and Hall effect in the ferromagnetic spinel \( \text{CdCr}_2\text{Se}_4 \) clearly show that these remarkable properties reflect changes in the density, not the mobility, of charge carriers [14]. These effects can be explained in terms of electron localization into entities roughly the size of a unit cell: i.e. MP. In fact, the MP concept now forms the basis for numerous studies of MS and related materials [22].

A magnetic polaron is formed by an electron localized due to its strong exchange interaction \( J \) with magnetic ions in its immediate environment, whose direct coupling is comparatively weak. Of relevance to the current study is the magnetic polaron (MP)—in which conduction electron transport for electrons in Si, GaAs, GaP and GaN is excellent, the effectiveness of prospective all-semiconductor spintronics devices is determined by the electron transport in doped magnetic semiconductors. These materials, however, can support states that lead to severe electron localization [14]. In fact, MS provide optimal conditions for the formation of a new type of quasiparticle—the magnetic polaron (MP)—in which conduction electron ‘autolocalization’ stabilizes an atomic-scale FM region well above \( T_c \) [20, 21, 14]. This electron localization in MS profoundly modifies their magnetic, electrical and optical properties. In particular, such MP determine most of the transport properties of magnetic semiconductors, leading to metal–insulator transitions with a remarkable resistivity change of up to 13 orders of magnitude (in doped EuO) and colossal magnetoresistance which suppresses resistivity by 3–4 orders of magnitude in magnetic fields of \( \sim 10 \) T [14]. Measurements of both resistivity and Hall effect in the ferromagnetic spinel \( \text{CdCr}_2\text{Se}_4 \) clearly show that these remarkable properties reflect changes in the density, not the mobility, of charge carriers [14]. These effects can be explained in terms of electron localization into entities roughly the size of a unit cell: i.e. MP. In fact, the MP concept now forms the basis for numerous studies of MS and related materials [22].

In treating the s–d(f) exchange interaction, two limiting cases are important: when the s-electron bandwidth \( W \) is large compared with \( J \), and when \( J \gg W \). The former case is typical for the s–f exchange in rare-earth compounds where the extremely localized f electrons are screened by electrons of other shells. In particular, in Eu compounds the s electron delocalized in the rather wide (a few electronvolt) hybridized 5d–6s band exchanges with the partially filled inner 4f shell, which is separated from the band states by completely filled 5s and 6p shells, thus reducing \( J \) to a few tenths of an electronvolt. The opposite case \( W \ll J \) provides the basis for the well-known double exchange in transition metal compounds. Perhaps surprisingly, this inequality is likely to be quite realistic in such compounds where the charge carriers are often of the same d type as the localized spins of the magnetic ions. In particular, the Fermi level in \( \text{CdCr}_2\text{Se}_4 \) falls in the middle of the narrow d band, which lies just below a much broader unoccupied s–p conduction band [32].

In this paper, we present experimental evidence of severe electron localization into a magnetic polaron bound to a positive muon in the paramagnetic phase of the 3d-electron magnetic semiconductor \( \text{CdCr}_2\text{Se}_4 \).

\( \text{CdCr}_2\text{Se}_4 \) is a chalcogenide spinel with cubic symmetry (56 atoms per unit cell), a lattice constant of 10.72 Å and a direct gap of about 1.5 eV. Its magnetic moment per chemical formula unit is close to 6 \( \mu_B \), which corresponds to the sum of two \( \text{Cr}^{3+} \) moments, each having a moment of 3 \( \mu_B \). Spontaneous ordering of the \( \text{Cr}^{3+} \) moments into the FM phase occurs at \( T_c = 130 \) K. Above \( T_c \), its paramagnetic susceptibility exhibits Curie–Weiss behavior.

Single crystals of \( \text{CdCr}_2\text{Se}_4 \) for the current study were grown by the closed-tube vapor transport technique. They all have perfect octahedral shape with typical sizes of 3–5 mm. They are slightly n-type with carrier concentrations of about \( 10^{15} \) cm\(^{-3} \) at room temperature. Magnetization (SQUID) measurements in \( H = 50 \) Oe were used to confirm \( T_c = 130 \) K for these crystals, in close agreement with literature data (figure 1).

Time-differential muon spin rotation/relaxation (TD-\( \mu^+ \)SR) experiments were carried out on the M15 surface muon channel at TRIUMF using the HiTime \( \mu^+ \)SR spectrometer. In a TD-\( \mu^+ \)SR experiment, one accumulates a time spectrum by detecting the arrival and subsequent decay of 100% spin-polarized 4 MeV positive muons stopped in the sample one at a time. The \( \mu^+ \)SR technique relies upon positrons from muon decay being emitted preferentially along the direction of the muon spin [26]. The resultant muon decay asymmetry directly reveals the time-dependent amplitudes of different characteristic precession signals which can be presented as a frequency spectrum (figure 2) or in the time domain (figure 3).
Figure 1. Temperature dependence of the magnetization of a CdCr$_2$Se$_4$ crystal measured using a SQUID magnetometer in a magnetic field of $H = 50$ G.

Figure 2. Frequency spectrum of muon spin precession in CdCr$_2$Se$_4$ in a transverse magnetic field of $H = 1$ T at $T = 300$ K. The two-frequency pattern (blue and red online), characteristic of the muon–electron bound state, occurs at frequencies higher than the narrower background signal.

In a high magnetic field applied transverse to the initial muon polarization, the TF-$\mu^+$SR spectra exhibit two Mu-like signals shifted to higher frequencies relative to the narrow line positioned exactly at the diamagnetic frequency $\nu_\mu = \gamma_\mu B / 2\pi$ (where $\gamma_\mu = 2\pi \times 135.54$ MHz T$^{-1}$ is the muon gyromagnetic ratio and $B$ is the magnetic field), as shown in figure 2. This narrow line is a background signal from muons stopped outside the sample; it provides a good reference since it does not depend on temperature. The two broader signals (blue and red online) at higher frequencies depend on both temperature and magnetic field and present a characteristic signature of the muon–electron bound state. For a $\mu^+e^-$ (Mu) spin system [as for $p^+e^-$ (Hi)] governed by the Breit–Rabi Hamiltonian, these signals correspond to two muon spin-flip transitions between states with fixed electron spin orientation [26].

Accordingly, the rotating reference frame (RRF) [26] fits of the $\mu^+$SR spectra in the time domain at various temperatures show three-frequency precession (1 background and 2 Mu-like signals, figure 3). The evolution of these signals is presented in the inset to figure 4. We claim that the two Mu-like lines are the spectroscopic signature of the magnetic polaron—one electron localized around the positive muon by the combined effects of Coulomb and exchange interactions. In CdCr$_2$Se$_4$ this muon-bound MP forms at temperatures well above $T_c$, up to at least 300 K. The shift of the centroid of the two-line MP spectrum, the splitting and the linewidths all scale with the bulk magnetic
susceptibility over the 160–300 K temperature range, implying a common origin: magnetic polarons and their orientational dynamics.

Similar two-frequency signals originating from magnetic polarons are detected in the 4f magnetic semiconductors EuS, EuO, EuSe [23] and SmS [24]. In all the MS studied, the MP lines are shifted with respect to the reference signal, reflecting the local ferromagnetic environment around the muon. In Eu chalcogenides, the MP lines exhibit negative shifts with respect to the reference signal, indicating that the MP electron spin is opposite to the net polaron spin. Addition of the MP electron effectively reduces the spin of the neighboring Eu ion from $7/2$ (according to Hund’s rule, the maximum allowed spin is for a half-filled f shell) to three due to Pauli exclusion. By contrast, in Cr spinels the MP electron is bound to have its spin parallel to the net MP spin (Hund’s rule for a less than half-filled d shell), which effectively increases the spin of one of the neighboring Cr ions from its original value of $3/2$ to $2$. Accordingly, in CdCr$_2$Se$_4$ the FM shift is positive (see figure 2). The absolute value of this shift at room temperature and 1 T is about 0.007 T.

The splitting $\Delta \nu$ between the two MP lines provides information on the muon–electron hyperfine coupling $A$, which is determined by the probability density of the electron wavefunction at the muon [26]. Figure 4 shows the temperature dependence of this splitting. A distinctive feature of magnetic semiconductors in general, and CdCr$_2$Se$_4$ in particular, is a strong dependence of the conduction electron energy on the magnetization, due to the exchange interaction between the mobile electron and localized d(f) spins, the minimum electron energy being achieved at the ferromagnetic ordering [14]. In the paramagnetic state, an ‘extra’ electron tends to establish and support this ordering, thus forming a FM ‘droplet’ (MP) over the extent of its wavefunction. The exchange contribution to the localization (see equation (1)) amounts to the difference between the paramagnetic disorder of the CdCr$_2$Se$_4$ and the enhanced (FM) order in the MP. In 3d magnetic semiconductors, the exchange interaction amounts to several tenths of an electronvolt [14], which (a) is comparable to the rather narrow d-electron bandwidth, ensuring compensation of the increase in the electron’s kinetic energy due to localization; and (b) ensures MP formation up to room temperature and above. For comparison, in 4f magnetic semiconductors the MP appears stable up to 500 K in EuS [35] and 850 K in SmS [24].

By contrast, in the FM state the exchange contribution to the localization is negligible, as the lattice spins are already aligned. In fact, as the magnetization develops toward low temperature, the exchange contribution to electron localization diminishes and therefore can no longer compensate the increase of its kinetic energy. The electron thus avoids strong localization as the temperature approaches $T_c$ from above. Accordingly, we do not detect the MP lines below about 150 K (see figure 4).

Temperature and magnetic field dependences of the MP signal frequency splitting $\Delta \nu$ provide information on the characteristic size (the localization radius for electron confinement) of the MP in CdCr$_2$Se$_4$. Since the Mu electron spin is ‘locked’ to the MP moment, the observed splitting scales with the mean orientation of the MP moment with respect to the external field, reaching the intrinsic Mu hyperfine constant only for complete alignment (see appendix of [23]). Amplitudes for the two-frequency spectrum qualitatively scale as expected for a bound electron whose spin is locked to that of the polaron core, providing strong support for this picture. Within a mean field approximation, $\Delta \nu$ is thus proportional to a Brillouin function [33, 23]. For $g \mu_B B \ll k_B T$, this function is linear in $B/(T - \Theta)$ (see figure 5):

$$\Delta \nu = A \left( \frac{g \mu_B B}{3k_B(T - \Theta)} \right) (S + 1),$$

where $\Theta = 140$ K is the paramagnetic Curie temperature of CdCr$_2$Se$_4$ and $S$ is the net polaron spin. At low $T - \Theta$ and/or high $B$, equation (2) is not valid any more, as the gigantic spin $S$ saturates [33, 23]. Therefore at $T = 200$ K $\Delta \nu$ deviates from a linear field dependence above about $H = 4$ T and levels off at a value of $A$ [26, 23–25]. Being one giant local spin, the MP interacts with magnetic ions of the environment, or, equivalently, is an object under the influence of a mean field, like any other spin in the system. Therefore the characteristic critical point of CdCr$_2$Se$_4$—its paramagnetic Curie temperature—enters into equation (2) explicitly. In EuS, the MP lines are detectable only at temperatures much higher than $T_c = 16$ K. Therefore, the analog of equation (2) is derived in the limit $T \gg T_c$ [23]. By contrast, in CdCr$_2$Se$_4$ (because of significantly lower magnetization than that in EuS) the polaron lines are detectable down close to the vicinity of $T_c$. Thus in equation (2) as applied to CdCr$_2$Se$_4$, $T$ in the denominator is replaced by $(T - \Theta)$ [23, 33].

The vacuum state of a Mu atom is characterized by its hyperfine coupling $A_{\text{vac}} = 4463$ MHz which corresponds to electron confinement within $R_{\text{bub}} = 0.0529$ nm. In a solid nonmagnetic medium, Mu usually has $A < A_{\text{vac}}$ so that, in a magnetic field high enough to satisfy $\gamma \mu_B B / 2\pi \gg A$, the splitting is $\Delta \nu = A$, independent of temperature and magnetic

**Figure 5.** Dependence of the splitting between MP lines on inverse temperature in a magnetic field of $H = 1$ T. Inset: magnetic field dependence of the same splitting at $T = 200$ K (circles) and $T = 300$ K (squares).
This value of $A$ gives a measure of the electron confinement around the muon at $T = 200$ K: assuming an expanded hydrogen-like MP wavefunction, the hyperfine coupling $A$ scales as $1/R^3$, where $R$ is the characteristic radius of the corresponding 1s electron wavefunction. We find $R \approx 0.3$ nm, which falls between the nearest neighbor (NN) and next nearest neighbor (NNN) ion coordination spheres. This value of $R$ is about an order of magnitude smaller than that calculated in [34] for temperatures just above $T_c$. It is known, however, that $R$ grows very fast as one approaches $T_c$ from above [14, 21]. The value of the MP spin extracted from the slopes of both linear dependences of $\Delta \nu$ on $T$ and $H$ at higher temperature and lower magnetic field (see figure 5 and the inset for $T = 200$ K) using equation (2) amounts to $S = 30 \pm 4$. This is reasonably consistent with a fully polarized core of 4 NN and 12 NNN Cr $^{3+}$ ions, yielding a net spin of 24, plus a partially ordered halo. The value of $S$ found in CdCr$_2$Se$_4$ lies within the range of MP net spins found in other magnetic semiconductors [23, 24] and is consistent with theoretical expectations [14, 21].

Here we find an important difference between MP in 4f and 3d MS: while in 4f MS the radius of the electron wavefunction is much less stringent because of the significantly larger spread of the 3d wavefunction. In CdCr$_2$Se$_4$, therefore, $R$ falls in between the NN and NNN Cr$^{3+}$ ions. More generally, exchange-driven electron localization in 3d magnets might enhance FM coupling between host magnetic ions by formation of MP around impurity atoms. In particular, in our CdCr$_2$Se$_4$ crystals, which are slightly n-type, bound MPs might possibly form around various donors. In $\mu$SR experiments, however, positive muons sample only a very local environment. Once the MP is formed around the muon, it effectively ‘screens’ the muon magnetic moment from interactions with any magnetic polarons formed around other impurities. The low concentration of such possible donor impurities ($\sim 10^{18}$ cm$^{-3}$ in our crystals) also makes it difficult to detect such MPs by different macroscopic magnetic techniques like SQUID magnetometry.

In conclusion, using the positive muon as a donor center we have generated and detected the model MP in CdCr$_2$Se$_4$. The characteristic radius of this MP is $R \approx 0.3$ nm. Exchange interactions governing MP formation may be important in understanding spin and charge fluctuation processes in materials of current interest.

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