Magnetic polaron bound to the positive muon in SmS: Exchange-driven formation of a mixed-valence state

Vyacheslav G. Storchak,[1,*] Jess H. Brewer,[2] Donald J. Arseneau,[3] Scott L. Stubbs,[2] Oleg E. Parfenov,[1] Dmitry G. Eshchenko,[4,5] Elvezio Morenzoni,[5] and Tel'man G. Aminov[6]

[1]*Russian Research Centre "Kurchatov Institute," Kurchatov Sq. 1, Moscow 123182, Russia*

[2]*Department of Physics and Astronomy, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Z1*

[3]*TRIUMF, 4004 Wesbrook Mall, Vancouver, British Columbia, Canada V6T 2A3*

[4]*Physik-Institut der Universität Zürich, CH-8057 Zürich, Switzerland*

[5]*SμS, Paul Scherrer Institute, CH-5232 Villigen, Switzerland*

[6]*Institute for General and Inorganic Chemistry, Moscow 119991, Russia*

(Received 20 April 2009; published 13 May 2009)

Muon spin-rotation experiments (supported by magnetization measurements) have been carried out in the canonical 4f mixed-valence narrow-gap semiconductor SmS from 10 to 900 K in magnetic fields up to 3.5 T. A bound state of an electron around a positive muon is found to form up to about 800 K. This state is a *magnetic polaron*: the electron wave function is confined within $R\approx 0.5$ nm (the first two coordination spheres) due to its exchange interaction with Sm magnetic moments. As such, it may serve as a model system for the hypothetical bound state suggested to account for a transition from divalent Sm^{2+} to trivalent Sm^{3+}, which is invoked to explain the transformation of SmS from a paramagnetic insulator into a magnetic metal at high pressure.

DOI: 10.1103/PhysRevB.79.193205 PACS number(s): 75.50.Pp, 71.22.+i, 75.50.Dd, 76.75.+i

The problem of spin and charge fluctuations close to a magnetic instability in mixed-valence (MV) systems has attracted considerable attention (see, e.g., Ref. 1 and references therein). In strongly correlated 4f electron systems, the class of MV materials known as narrow-gap semiconductors or Kondo insulators (SmB_6, YbB_{12}, TmSe, etc.) supports hybridization between localized 4f states and itinerant 5d-6s states causing instabilities in charge and magnetic configurations. These materials have been studied for almost four decades[2] but the mechanism of the valence fluctuation remains mysterious. Among them, the canonical MV system SmS makes an ideal material in which to study charge fluctuations in the vicinity of a quantum critical point because of the relative ease with which the Sm ion changes its ion charge state. Although a consensus has been reached that the remarkable properties of SmS may be understood in terms of a $Sm^{2+}(4f^6;J=0)\rightarrow Sm^{3+}(4f^5;J=5/2)+e(d,s)$ transition,[3] the mechanism of the electron capture/release remains a subject of current interest.

Unlike classical magnetic semiconductors (Eu chalcogenides, magnetic spinels, etc.) which experience metal-insulator transitions (MIT) close to the magnetic ordering temperature[4,5] at ambient pressure SmS remains a paramagnetic semiconductor within a NaCl crystal structure down to low temperature.[2] As the pressure is increased, SmS exhibits two successive phase transitions. First it undergoes an isostructural transition at the remarkably low pressure of $p_{BG}\approx 0.65$ GPa (at room temperature),[6] involving a valence change from a Sm^{2+} to a homogeneous mixed-valent (2.6–2.8) state.[2] This first-order phase transition is characterized by a huge volume collapse of up to 15% accompanied by a color change from black to golden.[7]

In the black phase, the Fermi level E_F falls into a gap between a $4f^6$ level and an unoccupied 5d band, thus making $Sm^{2+}S^{2-}$ a nonmagnetic narrow-gap semiconductor.[8] In the golden phase, the $4f^6$ level may be pushed into the conduction band,[8,9] resulting in a mix of divalent $4f^6$ and trivalent $4f^5$ configurations. In this phase the high-temperature resistivity is metallic but at low temperature the ground state is a strongly correlated semiconductor as long as the pressure is lower than $p_\Delta\approx 2$ GPa. Above p_Δ, the insulating gap closes resulting in metallic behavior down to low temperature and the onset of long-range magnetic order.[10,11] This constitutes the second phase transition.

It is expected that, at sufficiently high pressure, SmS would reach a trivalent state accompanied by the onset of long-range magnetic order since Sm^{3+} is a Kramers ion.[12] In fact, contrary to expectations, x-ray absorption measurements have revealed that the pure trivalent state is not a necessary requirement: the MV state exists both below and above the ordering temperature—at the onset of magnetic order the valence is $v=2.78(4)$.[12]

In any case, it is now accepted that SmS is insulating and divalent below p_{BG}, while the magnetic phase above p_Δ is metallic and eventually becomes trivalent at higher pressure. The crucial question then is whether a gap opens at E_F between p_{BG} and p_Δ—in other words, is one of the 4f electrons still bound to its parent Sm ion in the MV phase and if so, what is the nature of this bound state?

Experimental data so far are controversial: specific-heat measurements at 1.5 GPa indicated a heavy-fermion metallic state, while both resistivity and point-contact spectroscopy showed semiconducting properties.[2] These discrepancies arise from uncertainties in high-pressure experiments. In particular, there are notorious difficulties in controlling and correctly measuring pressure at low temperature.[8] Recent thermal expansion and heat-capacity measurements which carefully addressed these difficulties reported pseudogap formation between p_{BG} and p_Δ in the MV golden phase.[8] Furthermore, the authors proposed formation of a novel bound state between the insulating and the metallic phases suggesting that a valence-fluctuating electron is ejected from Sm^{2+} to be bound around its original Sm site. Formation of a bound state is also invoked to explain inelastic neutron-scattering spectra in MV materials.[13] However, the origin of this bound state remains to be identified. In the current Brief Report we address this problem.

The remarkable effect of "self-doping" in the semiconducting phase of SmS is relevant to this problem: the Sm $4f^6$ levels lie close to the bottom of the conduction band (activation energy $E_f=0.23$ eV at ambient pressure) and may act like donor levels.[14] At elevated pressure (close to p_{BG}) the $4f^6$ levels are pushed up to $E_f \sim 0.1$ eV.[15] The activation energy of defect Sm ions [even nominally stoichiometric single crystals contain $N_i \sim (10^{20}-10^{21})$ cm^{-3} of interstitial Sm] is $E_i=0.045$ eV at ambient pressure.[15] Thus the insulator-metal transition in SmS may be caused by screening of the Coulomb potential of the Sm ion by electrons ejected into the conduction band from both defect and $4f$ levels as pressure is increased. As the critical concentration of conduction electrons $n_k \sim N_i$ is reached one of the $4f$ electrons can no longer remain bound to the Sm^{2+} ion and SmS becomes a metal:[9] at room temperature, the carrier concentration shows a jump from 10^{20} to 10^{22} cm^{-3} at p_{BG}.[14]

In this model it is assumed that, as n_k is reached, a Mott-type phase transition is realized in the system of donor levels which are all simultaneously pushed up into the conduction band. Ejection of $4f$ levels accompanies the latter process, which causes the first-order transition in SmS. The criterion for such a transition is then that the Debye screening radius a_D of the Coulomb potential $\phi=(e/\epsilon r)\exp(-r/a_D)$ becomes smaller than the Bohr radius a_B of the corresponding state.

Within this model, however, neither Sm defect levels nor $4f$ levels can explain the experimental value of p_{BG}: the Bohr radius of the Sm impurity level (0.9 nm) is too large, while the strongly localized ground state of $4f$ levels is rather small (0.03 nm). The required value of about 0.3–0.5 nm prompted the authors of Ref. 9 to invoke the excited states of $4f$ levels.

However, this model does not take into account another source of electron localization, namely, the exchange interaction between electrons ejected into the conduction band and the magnetic moments of Sm^{3+} ions formed as a result of this injection. In this Brief Report we show that this exchange interaction may cause formation of the magnetic-polaron (MP) bound state in SmS with a characteristic radius of about 0.5 nm, as required to both reconcile the results of Ref. 9 with the experiment and support the idea of a hypothetical bound state invoked to describe the mysterious MV phase for pressures between p_{BG} and p_Δ.

The MP, a few-body state formed by a charge carrier (electron) localized due to its strong exchange interaction J with magnetic ions in its immediate environment whose direct coupling is rather weak,[4,5] is involved in the processes leading to insulator-metal transitions.[16] Of relevance to the current study is the so-called *bound* MP in which the increase in the kinetic energy of the electron (effective mass m^*) due to localization is expected to be compensated by the $s(d)$-f exchange interaction J combined with the Coulomb interaction with the corresponding donor so that the net change in the free energy

$$\Delta F = \frac{\hbar^2}{2m^* R^2} - J\frac{a^3}{R^3} - \frac{e^2}{\varepsilon R} \tag{1}$$

has a minimum as a function of R, the radius of the electron confinement.[4,17] In a system of magnetic ions, the electron energy depends strongly on the magnetization, the minimum electron energy being achieved at the ferromagnetic (FM) ordering.[5] For this reason the electron tends to establish and support this ordering thus forming a FM "droplet" over the extent of its wave function in a paramagnetic host.

In order to generate a MP in PM SmS, one has to populate its empty conduction band with a sufficiently low concentration of free carriers to ensure a strong unscreened Coulomb interaction. Instead of applying pressure, which is hard to control precisely, one can *inject* a low concentration of free carriers into the empty conduction band at ambient pressure from the ionization track of a high-energy (4 MeV) positive muon (μ^+) which may then act as a Coulomb center for electron localization (combined with the exchange interaction between the electron and Sm magnetic ions) to form the MP.

This technique has recently been demonstrated in the related EuS host[17] as well as in other magnetic semiconductors[18] following muon spin relaxation (μ^+SR) (Ref. 19) experiments in insulating[20,21] and semiconducting[22–25] media, which have shown that one of the excess electrons generated in the track can be captured by the muon to form a muonium ($\mathrm{Mu} \equiv \mu^+ e^-$) atom.

In semiconductors, the Mu atom thus formed produces a model system with which to study electron capture and release from the donor center since a positive muon acts in this respect just like any other Coulomb-attractive donor center.[25] In an array of magnetic ions the long-range Coulomb interaction ensures electron capture while the short-range exchange interaction provides further localization into an MP bound to the muon. Since the muon stops at the interstitial position in SmS,[26] the MP thus formed around the muon produces an ideal model system for the possible electron bound state around an interstitial Sm^{3+} ion which determines both the valence and the metallicity/magnetism in SmS.

Time-differential μ^+SR experiments with 100% polarized positive muons implanted into a polycrystalline SmS sample were carried out on the M15 and M20 surface muon channels at TRIUMF using the *LAMPF* and *Helios* spectrometers. In high magnetic field transverse to the initial muon polarization, the μ^+SR spectra exhibit two Mu signals on either side of the (absent) diamagnetic muon frequency—a characteristic signature of the muon-electron bound state.[19]

A typical μ^+SR spectrum in SmS is shown in Fig. 1. For a μ^+e^- spin system governed by the Breit-Rabi Hamiltonian,[19] these signals correspond to two muon spin-flip transitions between states with the same electron-spin orientation and the frequency splitting between these two signals is equal to the muon-electron hyperfine constant A.[19] A recent experiment in EuS (Ref. 17) has revealed a similar two-frequency signal interpreted as a Mu-like bound state (the magnetic polaron). In EuS there is an additional precession frequency from about half the muons which avoid electron capture. These diamagnetic states exist in EuS because

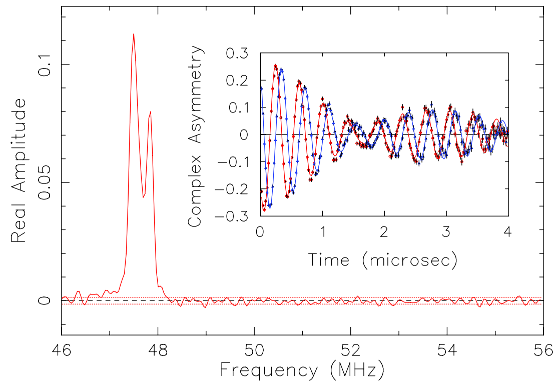

FIG. 1. (Color online) Frequency spectrum of muon spin precession in SmS in a transverse magnetic field of $H=0.35$ T at $T=40$ K. (Inset: time spectrum in rotating reference frame at 45 MHz.) The two-frequency precession pattern is characteristic of the muon-electron bound state.

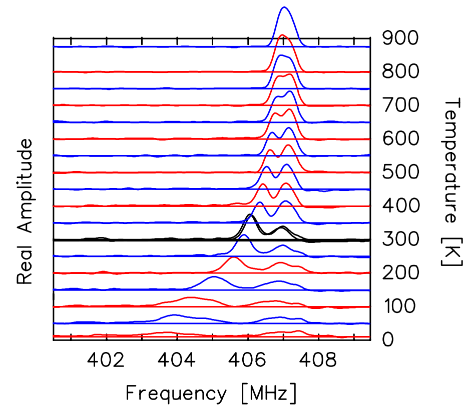

FIG. 2. (Color online) Fourier transforms of the muon spin precession signal in SmS in an external magnetic field of 3 T at different temperatures. Characteristic MP lines persist down to 10 K and up to 800 K.

its magnetization (measured by superconducting quantum interference device in both samples) is about an order of magnitude higher than in SmS, which diminishes the exchange term in the free energy [see Eq. (1)] making it too small to compensate for the increase in electron kinetic energy due to localization. In SmS, the low magnetization ensures 100% bound state formation—the exchange contribution to the localization amounts to the difference between the paramagnetic disorder of the SmS and the enhanced (FM) order in the MP. Accordingly, as the magnetization develops toward low temperature, the exchange contribution to the electron localization diminishes [see Eq. (1)] and the MP does not form at temperatures below about 90 K in EuS ($T_c=16.5$ K).[17] In contrast, SmS is paramagnetic down to the lowest measured temperatures and so is a very favorable host for MP formation: we found characteristic MP lines down to 10 K. Figure 2 presents the evolution of the MP signals in SmS with temperature. As the magnetization develops toward low temperature, both lines exhibit some negative shift since the magnetic field at the muon follows the bulk magnetization. This shift is much larger in EuS (Ref. 17) because of its much stronger magnetization.

The MP signal frequency splitting $\Delta\nu$ provides insight into the characteristic size and magnetic structure of this bound state through the muon-electron hyperfine coupling A and the composite spin $\mathcal{S}$ of the MP.[17] Within a mean-field approximation, $\Delta\nu$ is proportional to a Brillouin function.[27] For $g\mu_B B \ll k_B T$, it is a linear function of both B and $1/T$ (Ref. 17):

$$\Delta\nu = A\left(\frac{g\mu_B B}{3k_B T}\right)(\mathcal{S}+1). \tag{2}$$

However, at low T and high B the composite spin $\mathcal{S}$ is fully polarized and $\Delta\nu$ saturates at a value of A.[17,19] Figure 3 shows the MP frequency splitting in SmS as a function of both $1/T$ (in a magnetic field of $H=3$ T) and H (at room temperature).

Below about 100 K, $\Delta\nu$ starts to level off at $A\approx 3.5$ MHz. For a Mu atom with $A \ll A_{vac}=4463$ MHz (the hyperfine coupling of Mu in vacuum with $R=R_{Bohr}=0.0529$ nm), the value of A scales as $1/R^3$, where R is the characteristic Bohr radius of the corresponding 1*s* wave function. We find $R\approx 0.5$ nm, which contains 12 Sm ions with spin $\frac{5}{2}$ each in two coordination spheres of the SmS lattice around the muon. The composite spin of such an MP, when fully saturated, is $\mathcal{S}=30$. Using Eq. (2) we obtain a value of $\mathcal{S}=45\pm 5$ from both the slope of $\Delta\nu$ vs $1/T$ at high temperature (see Fig. 3) and the slope of $\Delta\nu(B)$ (see inset of Fig. 3). This is consistent with a fully polarized core plus a halo of magnetically unsaturated ions. For comparison the analogous MP in EuS has $R\approx 0.3$ nm which encloses four Eu ions of spin $\frac{7}{2}$ each in just the first coordination sphere[17] with a composite spin $\mathcal{S}=36\pm 4$ of the fully polarized core and the halo region of enhanced magnetic moment.[17]

Since the positive muon[26] and the Sm^{3+} ion[15] both adopt an interstitial position in SmS, the observed MP may serve as a model for the hypothetical bound state around native Sm^{3+} ions proposed[8] to account for MV behavior in SmS. Furthermore, since the 4*f* electron is strongly (0.03 nm) localized,[9,14] the 4*f* hole on the Sm^{3+} ion behaves as a point-like defect similar to the positive muon. The characteristic

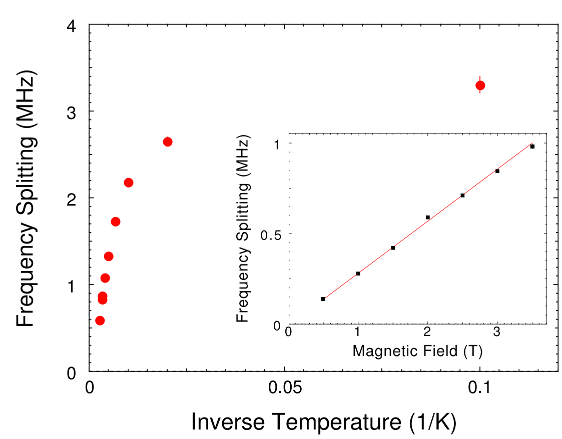

FIG. 3. (Color online) Temperature dependence of the MP frequency splitting $\Delta\nu$ in SmS in a magnetic field of $H=3$ T. Inset: magnetic-field dependence of $\Delta\nu$ at $T=297$ K.

radius a_B of a bound state at a Mott-type MIT under pressure can be roughly estimated from $a_B \times n_k^{1/3} \approx 0.2-0.4$ giving $a_B \approx 0.25-0.45$ nm, since $n_k \approx 8 \times 10^{19}$ cm^{-3} in SmS at 300 K at MIT.[14] This value is consistent with $R \approx 0.5$ nm found for the MP bound to the muon in SmS.

More generally, a partially delocalized[28] or weakly bound electron is assumed in "local bound-state" models of mixed valence.[29,30] Exchange-driven electron wave-function confinement on the scale of a lattice spacing may be an important missing ingredient in the description of MV materials.

In conclusion, using the positive muon as a donor center we have generated and detected the model MP in SmS. The characteristic radius of this MP is $R \approx 0.5$ nm. Exchange interactions governing MP formation may be important in understanding spin- and charge-fluctuation processes in materials of current interest.

This work was supported by the Kurchatov Institute, the Canadian Institute for Advanced Research, and the Natural Sciences and Engineering Research Council of Canada.

*mussr@triumf.ca

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