Pressure-Induced Magnetic Order in Golden SmS

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High pressure ^{149}Sm nuclear forward scattering experiments have been performed on the nonmagnetic semiconductor SmS. We present the first clear evidence that the closure of the insulating gap at $p_\Delta \approx 2$ GPa coincides with the appearance of magnetic order. The pressure-induced magnetic phase transition has some first order character and suggests that the Sm ions are nearly trivalent at p_Δ. A Γ_8 quartet crystal field ground state with a value of $\sim 0.5\mu_B$ for the samarium magnetic moment is inferred from our results. Considerable magnetic short range order is observed above the ordering temperature inferred from macroscopic measurements.

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The class of strongly correlated $4f$ electron systems known as Kondo insulators or narrow-gap semiconductors has attracted considerable interest recently. In their high temperature state these systems are believed to consist of a lattice of uncorrelated $4f$ ions, each independently scattering conduction electrons by the Kondo mechanism. At low temperatures correlations exist and the ground state is semiconducting with a small gap. These semiconductors exhibit the features characteristic of intermediate valence (IV) phenomena studied three decades ago [1]. Among them, SmS has received in the past much attention due to its valence and semiconductor to metal transitions at an incredibly low pressure (0.65 GPa at room temperature) [2–4]. Despite these efforts, very fundamental aspects were left unsettled at that time. The development of new generations of experiments, including high pressure techniques, as well as the advances made in electronic structure calculations now make it possible to revisit the electronic and magnetic properties of the key compound SmS with the aim to gain new insights into its pressure-temperature (p, T) phase diagram.

At ambient pressure SmS is a nonmagnetic semiconductor (black phase) where the samarium ions are divalent ($4f^6$:$^7F_0$). At $p_{B-G} \sim 0.65$ GPa and room temperature (RT) it undergoes a pressure-induced isostructural (NaCl-type) first order transition towards a metallic phase (gold phase) with a large volume collapse (~8%). Gold SmS is in a homogeneous mixed valence state with a Sm valence, just after the transition, ranging from 2.6 to 2.8 depending on the experimental technique used [1]. The temperature dependence of the electrical resistivity shows, however, that the ground state of the gold phase is a semiconductor and that the insulating gap closure, i.e., metallic behavior down to low temperature, is observed only above $p_\Delta \approx 2$ GPa [3,4]. Similar features were also reported for other IV compounds such as SmB_6, YbB_{12}, and TmSe [1]. An interesting question concerns the behavior of the IV nonmagnetic ground state of SmS as a function of pressure and its possible crossover into the trivalent ($4f^5$:$^6H_{5/2}$) magnetic state at a critical pressure p_c. The room temperature pressure dependence of the samarium valence (v) was investigated by L_{III} absorption measurements. They show that v increases nonlinearly above p_{B-G} reaching a value of $v \approx 2.9$ at 7.2 GPa [5]. From the pressure effect on the lattice parameters at RT it was suggested that normal trivalent behavior could be observed only above 10 GPa [6]. Recent specific heat measurements [7] show the appearance of a phase transition for $p \gtrsim 2$ GPa. This and the anomaly seen in the electrical resistivity [8] do not provide direct proof that they are of magnetic origin, although the electronic structure calculated in the local spin-density approximation including correlations predicts a magnetic ground state for the SmS high pressure gold phase [9].

In this Letter, we present clear evidence that above p_Δ the collapse of the insulating gap coincides with the appearance of magnetic ordering. This result was obtained by performing ^{149}Sm high pressure nuclear forward scattering (NFS) of synchrotron radiation for the first time. From these measurements we obtained information about the magnetic hyperfine field at the ^{149}Sm nuclei as a function of pressure and temperature. The data show that at about 2 GPa a likely first order transition occurs from the nonmagnetic IV state into a magnetically ordered state with a saturated moment of $\sim 0.5\mu_B$ stable to at least 19 GPa. The magnetic ordering temperature increases smoothly with p and its value at low pressure is in the range expected from comparison with other monosulphides with trivalent rare-earth ions [10]. Our findings strongly support the idea that already at p_Δ the Sm ions are nearly trivalent with a Γ_8 quartet crystal field ground state.

The SmS sample was prepared using isotopically enriched (97%) metallic ^{149}Sm. Samarium was prereacted with sulphur in a silica tube under vacuum using a conventional furnace. Tiny crystals were then grown by the Bridgman method in a tantalum crucible. The sample was checked by x-ray diffraction and found to be single phase (NaCl-type). High pressure, measured with the ruby fluorescence method at RT, was applied to a powdered sample using the diamond anvil cell (DAC) technique. Nitrogen was the pressure transmitting medium. The ^{149}Sm NFS measurements (resonant energy $E_0 =$ 22.494 keV; 5/2-7/2 transition) were performed at the undulator beam line ID22N of the European Synchrotron Radiation Facility, Grenoble, France. The energy bandwidth of the undulator radiation was reduced in two steps to $\Delta E \approx 0.9$ meV by a high heat-load monochromator followed by a nested high-resolution monochromator using a combination of Si(8 0 0) and Si(16 8 8) reflections. The beam was focused by a sagittally bent crystal to a spot matching the size of the sample in the DAC. This was mounted in a liquid helium cryostat. The scattered radiation was measured by using four stacked avalanche photodiodes [11].

NFS is a technique related to the Mössbauer effect; thus, similar microscopic information to that inferred from conventional Mössbauer spectroscopy can be obtained. This allows one to determine the pressure dependence of the magnetic hyperfine field B_{hf} of the ordering temperature T_m and of the principal component of the electric field gradient (EFG) V_{zz} at the ^{149}Sm nuclei. The change of the EFG with p is obtained from the pressure dependence of the electric quadrupole splitting $\Delta E_Q = eV_{zz}Q_g$, where Q_g is the nuclear quadrupole moment of the $I_g = 7/2$ ground state. Figure 1(a) shows some selected ^{149}Sm NFS spectra collected for SmS up to 19 GPa and at 3 K. As shown in the figure, at 1.73 GPa one observes a spectrum characteristic of unsplit nuclear levels; i.e., quadrupole or magnetic interactions are absent. The Sm ions are thus in a nonmagnetic state and, as expected for a NaCl-type structure, in a cubic symmetry. At 2.35 GPa, the spectral shape changes significantly and shows quantum beats indicating that the nuclear levels are now split by hyperfine interactions. The best fit to the data is obtained by assuming a superposition of well defined nonmagnetic and magnetic components with relative weights of about 28% and 72%, respectively. The data analysis was performed with the package MOTIF [12,13] by using the full dynamical theory of nuclear resonance scattering, including the diagonalization of the complete hyperfine Hamiltonian. Values of 261(10) T and $-1.50(6)$ mm/s (see Fig. 2) were deduced for the magnetic hyperfine field B_{hf} and the induced quadrupole interaction ΔE_Q, respectively, assuming that V_{zz} and

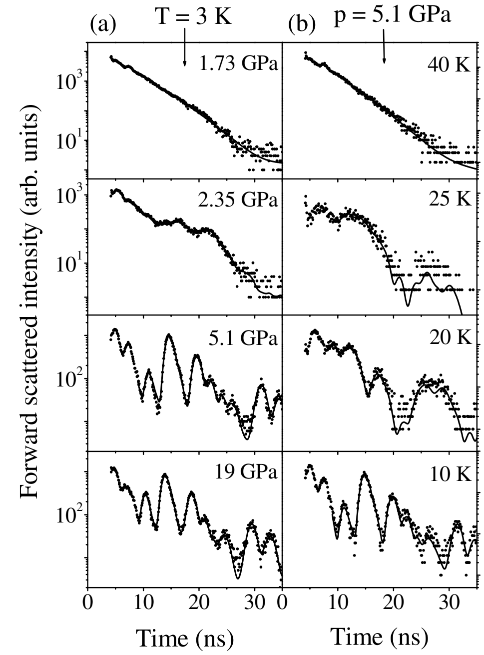

FIG. 1. ^{149}Sm NFS spectra of SmS: (a) at $T = 3$ K for some selected pressures and (b) at $p = 5.1$ GPa and different temperatures. The dots represent experimental data points, while the lines are fits.

B_{hf} are parallel [14]. By further increasing the pressure, the magnetic component in the NFS spectra grows at the expense of the nonmagnetic one, and at $p = 5.1$ GPa and 3 K all the Sm ions feel combined magnetic and quadrupole interactions with $B_{hf} = 284(10)$ T and $\Delta E_Q = -1.56(6)$ mm/s. Up to 19 GPa, the highest achieved

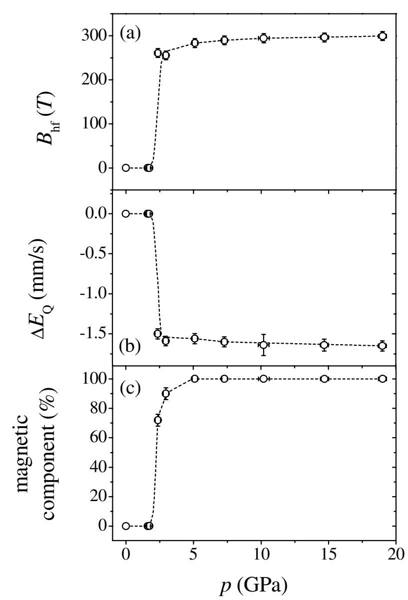

FIG. 2. Pressure dependences of (a) the magnetic hyperfine field (B_{hf}), (b) the quadrupole splitting (ΔE_Q), and (c) the magnetic component fraction at $T = 3$ K. The dashed lines through the data points are guides to the eye.

pressure, one observes only a slight increase of the hyperfine parameters [$B_{hf} = 299(10)$ T and $\Delta E_Q = -1.65(6)$ mm/s; see Fig. 2].

The pressure dependences of B_{hf}, ΔE_Q, and of the magnetic component fraction at 3 K (see Fig. 2) evidence a pressure-induced phase transition at $p_c \approx 2$ GPa from a nonmagnetic state to a magnetically ordered state. The steep variation of both B_{hf} and ΔE_Q as well as the coexistence of the low and high pressure phases in the vicinity of p_c point towards a transition that possesses a strong first order character. At this stage a second order transition cannot, in principle, be discarded. In order to discuss the properties of this state we will implicitly assume that p_c coincides with p_{3+}, the critical pressure where the Sm ions become trivalent or nearly so. Both B_{hf} and ΔE_Q are key parameters to characterize the ordered state because they are directly related to the wave function of the $4f$ electrons which, in general, involves contributions arising from the mixing of the ground multiplet ($^6H_{5/2}$) with excited states ($^6H_{7/2}, \ldots$) of the Sm^{3+} ions [15]. The values of both B_{hf} and ΔE_Q, for $p > p_c$, are significantly reduced compared to the Sm^{3+} free ion values of 338 T and -2.1 mm/s, respectively [17]. These reductions could be attributed to the crystal field of cubic symmetry acting on the Sm^{3+} ions and/or to the Kondo screening of the Sm local moment. The latter possibility is, however, difficult to reconcile with the very weak pressure dependence of B_{hf} and ΔE_Q in the large pressure range $2 \leq p \leq 19$ GPa. Indeed, the characteristic energy for the Kondo effect is expected to decrease with increasing pressure as in Yb-based Kondo lattices ($4f^{13}$, Yb^{3+}) where pressure enhances magnetism [18,19]. The cubic crystal field can therefore be considered as responsible for the reduced values of B_{hf} and ΔE_Q. However, an obvious difficulty to fully explain the behavior of the Sm ions in SmS is the proper estimation of the crystal field parameters $A_4\langle r^4\rangle$ and $A_6\langle r^6\rangle$. Taking into account the rather modest ordering temperature observed for SmS (see below), it appears sound to assume that in this case the exchange and crystal field interactions do not lead to a significant admixture between the ground ($^6H_{5/2}$) and the first excited ($^6H_{7/2}$) multiplet [20]. The lowest multiplet $^6H_{5/2}$ for the $4f^5$ configuration of the Sm^{3+} ions is split into a Γ_7 doublet and a Γ_8 quartet [21]. Inelastic neutron scattering experiments on PrS [22] and scaling of these results with the fifth power of the lattice parameter of SmS led to the conclusion that the Γ_7 doublet should be the ground state and that the Γ_8 quartet should lie at about 100 K in SmS [23]. However, neither inelastic neutron scattering (in the intermediate valence state [24]) nor resistivity measurements (in the gold phase above and below p_c [3,4,7,8]) gave any evidence for crystal field excitations. The former observation is common for systems where the hybridization effects smear out the crystal field states [25]. The absence of any additional peak or shoulder in the resistivity curves for $p > p_c$ suggests that the crystal field splitting Δ_{CF} (Γ_7-Γ_8 separation) amounts at most to the temperature value of the resistivity maximum (~20 K). This rather low crystal field splitting compared to the standard behaviour (~100 K) is tentatively ascribed to hybridization effects which, as shown experimentally [26] and theoretically [27] for CeSb, can reduce considerably Δ_{CF} and even lead to a Γ_8 ground state. We can compare the experimental B_{hf} and ΔE_Q values with those expected for either a Γ_7 (113 T and ~0 mm/s) or a Γ_8 (250 T and -1.7 mm/s) crystal field ground state. It follows that the NFS data are consistent with the occurrence of a Γ_8 quartet ground state, i.e., that the Sm ions carry a magnetic moment of $\mu_{Sm} \approx 0.5\mu_B$. A possible confirmation of this finding could be obtained by performing neutron form factor measurements at $p > p_c$ (see, for example, Ref. [26]).

In order to construct a magnetic phase diagram for SmS in (p, T) space, we have determined the pressure dependence of the ordering temperature T_m by measuring the temperature dependence of B_{hf} at different pressures. Figure 1(b) displays the temperature dependence of the NFS spectra at $p = 5.1$ GPa for $T \leq 40$ K. At 40 K the NFS spectrum presents the characteristic shape expected for paramagnetic Sm ions in a cubic environment. At lower temperatures the observation of quantum beats indicates the presence of combined quadrupolar and magnetic hyperfine interactions. Good fits to the data cannot be obtained with a single set of B_{hf} and ΔE_Q values. The spectral shape can be accounted for by allowing distributions of both B_{hf} and ΔE_Q whose widths decrease with decreasing temperature (even at 3 K a small spread of B_{hf} of ~3% is observed). The T_m values deduced from the analysis of the NFS spectra are shown in Fig. 3. They are significantly higher than those inferred from specific heat or resistivity measurements [7], which represent the onset temperature for long range magnetic order (LRMO). These observations clearly demonstrate that considerable short range magnetic order exists within the Sm sublattice: the interactions within this sublattice will give rise to spin motions whose rates are relatively slow as

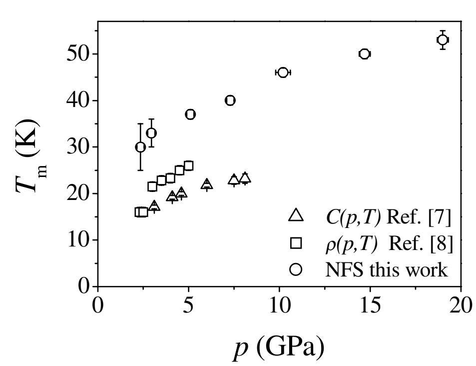

FIG. 3. Pressure dependence of the magnetic ordering temperature T_m of SmS as obtained from high pressure ^{149}Sm NFS measurements (circles) in comparison with the values inferred from high pressure resistivity (squares) and specific heat (triangles) measurements.

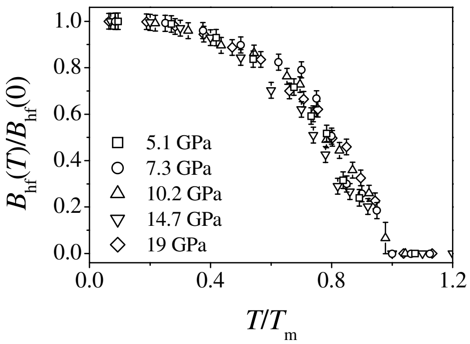

FIG. 4. Reduced hyperfine field as a function of the reduced temperature for different pressures.

compared to the Larmor frequency ($\sim 10^{10}$ s^{-1}) [28]. Figure 4 shows that the reduced hyperfine field $B_{hf}(T)/B_{hf}(0)$ as a function of the reduced temperature T/T_m for different pressures falls roughly on the same curve. Moreover, no clear anomalies are observed at the temperatures where LRMO sets in. At this stage no conclusion can be drawn on the possible magnetic structures of SmS. The model we used to take into account "broadened" spectral shapes may be oversimplified (the broadenings may be due to relaxation effects as well as to a distribution of hyperfine parameters). The possibility of an incommensurate structure cannot be ruled out, although simple type I or II antiferromagnetic structures are generally found in rare-earth chalcogenides [10]. Finally, one should emphasize that the magnetic ordering temperatures (LRMO) inferred from calorimetry and transport measurements [7] at low pressure fall in the range expected from de Gennes scaling of the ordering temperatures of other monosulphides with trivalent rare-earth ions (see review in Ref. [10]).

In summary, we have used ^{149}Sm NFS experiments to investigate the effect of pressure on the ground state properties of SmS which is located close to an electronic instability (valence, lattice, metal-insulator transition). We find that at $p_c \approx 2$ GPa SmS undergoes a transition from a nonmagnetic state to a magnetically ordered state with $\mu_{Sm} \approx 0.5\mu_B$. The transition has some first order character and our results at $p > p_c$ can be interpreted in the frame of trivalent Sm ions with a Γ_8 quartet crystal field ground state. The magnetic state we observe above 2 GPa is stable up to at least 19 GPa, our highest measured pressure. The comparison of our data with those inferred from calorimetry and resistivity measurements indicates that considerable dynamic short range magnetic order develops below about $2T_m$ (where T_m is the ordering temperature deduced from the macroscopic experiments). We think that our results should stimulate further experimental [e.g., precise determination of the valence in (p, T) space, search for magnetic Bragg peaks either by neutron or magnetic x-ray scattering] and theoretical efforts (evaluation of the magnetic ground state in the high pressure golden phase).

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