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Probing the (p, T) phase diagram of $CeFe_2$ and SmS using resonant x-ray scattering

P P Deen[1,5], L Paolasini[1], N Kernavanois[1,2], D Braithwaite[3], S Raymond[3], A Barla[1,3], G Lapertot[3], J P Sanchez[3] and P Canfield[4]

[1] European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble, France
[2] Institut Laue-Langevin, BP156, F-38042, Grenoble, France
[3] Département de Recherche Fondamentale sur la Matiére Condensée, SPSMS, CEA Grenoble, F-38054 Grenoble, France
[4] Ames Laboratory, Iowa State University, Ames, IA 50011, USA

E-mail: deen@esrf.fr

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Abstract

Two strongly correlated electron systems $CeFe_2$ and SmS have been studied using x-ray magnetic resonant scattering at low temperatures and high pressures. First, the magnetic ground state of $CeFe_2$ doped with 7% Co has been probed by means of resonant x-ray magnetic scattering across the temperature range 10–95 K at pressures up to 9.5 kbar. A strong increase of the Néel temperature with pressure has been evidenced. Furthermore, a large increase in scattering intensity is observed just before T_N at 9.5 kbar. These results reveal that the itinerant character of the 4f electrons which stabilize the antiferromagnetic state has been probed. Secondly, the structural and electronic properties of SmS have been studied under pressure up to 29 kbar and at temperatures down to 4.5 K via absorption and diffraction techniques. The measurements are a direct probe of the valence of Sm in SmS at low temperature from the black insulator phase to the gold metallic phase and furthermore across the magnetic transition. In particular, it is found that Sm in SmS has an intermediate valence (2.81(4)) in the magnetically ordered phase at 29 kbar and 4.5 K.

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

Resonant x-ray scattering is a very powerful tool for the comprehension of magnetic interactions and order. It complements and enhances information gained by neutron scattering techniques through the high Q-resolution and chemical and shell selectivity by using the energy tunability and the linear polarization analysis of synchrotron radiation [1]. Of particular interest

[5] Author to whom any correspondence should be addressed.

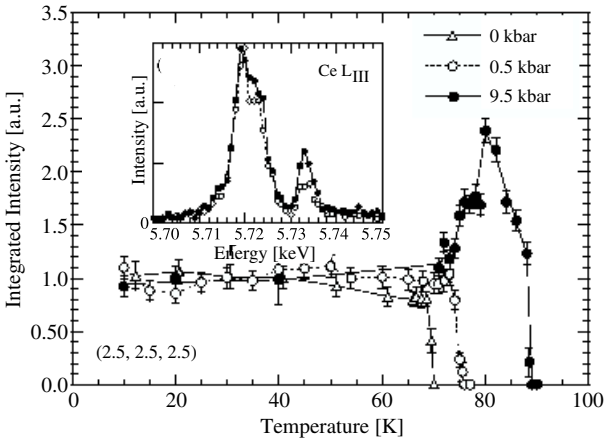

Figure 1. Temperature dependence for $Ce(Co_{0.07}Fe_{0.93})_2$ of the resonant magnetic x-ray scattering ($E = 5.720$ keV) at the $(\frac{5}{2}, \frac{5}{2}, \frac{5}{2})$ antiferromagnetic Bragg reflection with various pressures in the σ–π polarization channel. The inset shows the energy dependence of the resonant magnetic scattering across the Ce L_{III} absorption edge.

are the issues of spin and charge fluctuations close to a magnetic instability in mixed valence systems. A most remarkable breakthrough was the discovery of superconductivity close to the magnetic quantum critical point (QCP) for several heavy fermion compounds [2]. By applying pressure it is possible to tune the magnetic properties around a QCP. The study of such strongly correlated electron systems (SCES) will thus benefit greatly from the combination of resonant x-ray diffraction at low temperatures and high pressures. A novel set-up has recently been implemented on ID20 [3], the resonant magnetic scattering beamline of the European Synchrotron Radiation Facility (ESRF, Grenoble, France), that enables *in situ* pressure changes up to 30 kbar in the temperature range 1.5–300 K. A detailed description of this new set-up is reported in [4]. This paper outlines experimental results on two SCES compounds. First, resonant x-ray magnetic scattering (RXMS) results on Co doped $CeFe_2$ are discussed. Secondly, recent x-ray absorption and diffraction results on SmS are presented. Conclusions and perspectives will thereafter be given.

The rare earth iron phase of composition $CeFe_2$ contrasts greatly with other RFe_2 (R = rare earth) compositions due to the strong hybridization of the Ce valence band with the Fe 3d electrons [5]. The ground state of the pure Laves-phase compound $CeFe_2$ is ferrimagnetic with coexisting short range antiferromagnetic fluctuations [6]. However, doping with 7% Co stabilizes a non-collinear antiferromagnetic ground state with a first-order transition at $T_N = 69$ K and an ordering wavevector $\mathbf{Q} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ [7].

A $Ce(Co_{0.07}Fe_{0.93})_2$ single crystal, grown by flux growth [8], has been polished to obtain the desired size, $500 \times 200 \times 100\ \mu m^3$. The electronic state of Ce has been probed by RXMS at 0, 0.5 and 9.5 kbar as a function of temperature. Magnetic scattering was measured as a function of pressure around the Ce L_{III}, $E = 5.720$ keV, absorption edge using a LiF (2 2 0) crystal for polarization analysis.

Figure 1 reveals the temperature dependence of the resonant magnetic scattering intensities in the σ–π polarization channel of the $(\frac{5}{2}, \frac{5}{2}, \frac{5}{2})$ antiferromagnetic Bragg reflection with increasing pressures. The application of 0.5 kbar results in an increase of 5 K in T_N. Further increasing the pressure to 9.5 kbar results in a large increase of the Néel temperature ($T_N = 89$ K) and a huge intensity increase before the transition occurs. The latter result is

still under investigation. X-ray magnetic scattering at the $\mathbf{Q} = (\frac{5}{2}, \frac{5}{2}, \frac{5}{2})$ reflection around the Ce L_{III} absorption edge (see the inset of figure 1) shows the particular energy dependence due to the mixed valence character of the 4f electrons through the core–hole screening effects of the 5d band. These results prove the itinerant character of the Ce 4f and 5d electrons which stabilize the antiferromagnetic state by promoting the hybridization between the Fe and Ce itinerant electrons [9].

These first results revealed the feasibility of RXMS under pressure at low temperatures and opened the possibility to study other SCES. Among these, SmS is of particular interest. At ambient pressure SmS is a semiconductor that crystallizes in the NaCl structure with divalent Sm [10]. A small increase in pressure (6.5 kbar) at room temperature is sufficient to induce a well-known volume collapse of about 15% [11]. This first-order isostructural phase transition alters the valence state of Sm to a homogeneous, intermediate valence state [11–13] and the colour of the sample from black to gold. In the high pressure (gold) phase the resistivity at high temperature is metallic, but on lowering the temperature a crossover to a strongly correlated semiconductor is observed. This is only suppressed with pressures above approximately 20 kbar [14, 15]. Recent nuclear forward scattering results have shown that a further increase in pressure, to 20 kbar, gives rise to magnetic order below $T_N = 10$ K [16].

The phase diagram for SmS is as yet not well established. McWhan *et al* [17] performed a single measurement on the lattice parameter at 85 K and concluded that the transition pressure increased by 1 kbar with respect to ambient temperature. Further information on the black to gold transition has been gained by some resistivity measurements although the determination of the transition pressure at these temperatures is not obvious and different authors have extracted different values from the same data set [18, 13]. The valence state of the magnetic phase has not been probed. Since Sm^{3+} is a Kramers ion, it is expected that Sm in SmS will be trivalent at the emergence of magnetic order. The aim of this work was therefore to further establish the SmS (p, T) phase diagram in terms of the valence and structural transitions and their association with the semiconducting/metal and magnetic transitions.

A single-crystal SmS sample grown by the Bridgman technique has been cleaved to produce the required dimensions, $60 \times 110 \times 280\ \mu m^3$. In this study, the lattice parameters were measured at 4.5 K from the (0 0 4) structural Bragg peak. The [0 0 1] scattering plane was employed since platelets with this orientation are easily cleaved in SmS. The initial aim was to cross the black/gold boundary at 4.5 K but for mechanical reasons this was unsuccessful. Instead it was necessary to increase the temperature to 58 K in order to attain a pressure of 11.3 kbar and so reach the transition. Thereafter it was possible to cool to 4.5 K without loss of pressure. This provides a new point on the phase diagram and is an indication that the first-order transition is coincident with the analysis of the resistivity measurements by Morillo *et al* [18]. On crossing the transition an isostructural volume collapse of 13% was observed—see figure 2—and although the sample remained a single crystal, the mosaicity increased substantially from 0.030(2)° to 2.5(1)°. Below the transition, $p < 11.3$ kbar, a single Bragg peak was observed corresponding to the black phase. As the transition was crossed two peaks were resolved showing the phase separation within the sample. At higher pressures a single peak remained, implying the occurrence of an homogeneous mixed phase. As the pressure is further increased a uniform volume contraction is observed. No discontinuous volume contraction, as expected with the onset of magnetic order with trivalent Sm, was observed. This is in accordance with an intermediate valence state for Sm.

Absorption spectra obtained in the fluorescence yield configuration around the Sm L_{III}, $E = 6.716$ keV, absorption edge reflect the valence state of Sm in SmS [19]. The raw fluorescence spectra have been normalized to the incident beam monitor and corrected for background intensity below the white line and normalized to unity above the white line. A

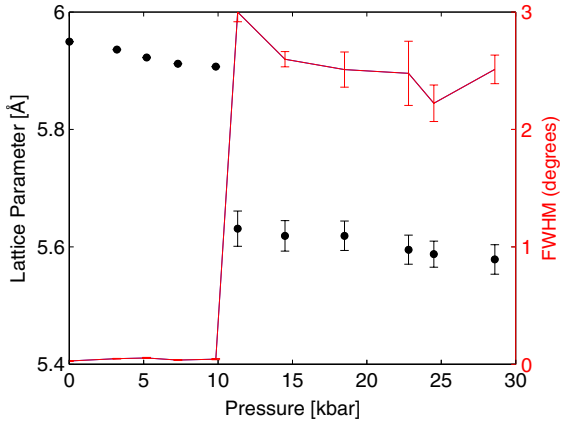

Figure 2. Lattice parameters and corresponding mosaicity obtained from the (0 0 4) structural Bragg reflection as a function of pressure at 4.5 K.

self-absorption correction in accordance with Pfalzer *et al* [20] was furthermore applied to obtain the absorption spectra. The valence state was then extracted in accordance with Rohler *et al* [19].

Figure 3(a) shows the absorption spectra across the Sm L_{III} absorption edge with increasing pressures at 4.5 and 50 K. As expected, a single white line at $E = 6.712$ keV is apparent at ambient pressure and indicates the divalent state of Sm in SmS. The divalent state remains until 11.3 kbar when the absorption spectrum dramatically changes and reveals a dominant trivalent white line at $E = 6.719$ keV. An increase in pressure reduces the relative intensity of the divalent white line with respect to the trivalent white line. Nevertheless, there is still an extensive divalent shoulder at 28.6 kbar indicating that Sm has not yet reached its trivalent state. The pressure variation of Sm implies that Sm in SmS will not become trivalent until at least 60 kbar. The extracted valence states are presented in figure 3(b). Below the transition a single white line in the absorption spectra indicates a uniquely divalent state. This is not necessarily accurate since analysis of the data reveals that any valence up to 2.2 would appear as divalent. The continuum behind the divalent white line would obscure the small contribution of the trivalent white line. Hence, it is not possible to verify the claim by Röhler *et al* [19] that a non-integer valence state exists below the semiconducting/metal transition. Above the transition, which was reached at 11.3 kbar and 58 K, the valence increases linearly with pressure. The electronic state of Sm as magnetic order is established shows no discontinuity and, contrary to expectation, magnetic order exists with intermediate valence Sm. The valence state at the onset of magnetic order extracted from this work is 2.78 ± 0.04. This agrees with the band structure calculations by Antonov *et al* where a low moment magnetic ground state exists in the low temperature golden phase of SmS with Sm in an intermediate valence state of 2.86 [21].

To conclude, the 4f and 5d electrons of Ce in $Ce(Co_{0.07}Fe_{0.93})_2$ have been probed and prove the itinerant character of these electrons which stabilize the antiferromagnetic state. Several features were observed. First, the Neél temperature increases with the application of pressure. Secondly, an unusual increase in scattering intensity is observed with the application of 9.5 kbar at temperatures above T_N found for $p = 0.5$ kbar. Further investigations are required to elucidate these features. As regards the study of SmS, a greater understanding of the (p, T) phase diagram has been gained from absorption spectra and x-ray diffraction measurements at the Sm L_{III} absorption edge. In particular it has been possible to map the

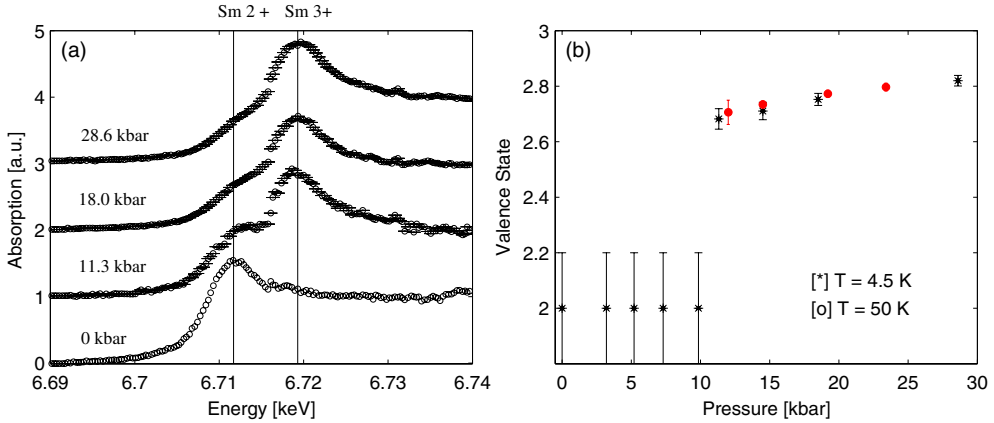

Figure 3. (a) Absorption spectra obtained in the fluorescence yield mode around the Sm L_{III} absorption edge at $T = 4.5$ K and with increasing pressure. The intensities are staggered to aid the eye. (b) The valence of Sm in SmS extracted from the absorption spectra in accordance with Rohler *et al* [19].

valence state of Sm in SmS and the structure of SmS by means of *in situ* pressure increases at 4.5 K up to 29 kbar. The structural and electronic states both experienced a first-order phase transition at 11.3 kbar and 58 K in this work. These data provide the first point on the transition curve from structural measurements and confirm the trend obtained from resistivity measurements [18]. The electronic state of Sm, as magnetic order is established, shows no discontinuity and, contrary to expectation, magnetic order exists for intermediate valence Sm. In particular the valence state of Sm in SmS in the magnetic phase at the highest pressure reached, 29 kbar and 4.5 K, is 2.81(4). It is hoped that further measurements will provide the precise details of the magnetic order. The possibility of performing resonant scattering under high pressure and low temperature regimes has opened a new window in the study of strongly correlated electron systems. This set-up can easily be used with most x-ray spectroscopic techniques (resonant inelastic scattering, circular dichroism, EXAFS) where low absorption and low temperature conditions are required.

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