Valence and magnetic instabilities in Sm compounds at high pressures

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Abstract

We report on the study of the response to high pressures of the electronic and magnetic properties of several Sm-based compounds, which span at ambient pressure the whole range of stable charge states between the divalent and the trivalent. Our nuclear forward scattering of synchrotron radiation and specific heat investigations show that in both golden SmS and SmB_6 the pressure induced insulator to metal transitions (at 2 and $\sim$4–7 GPa, respectively) are associated with the onset of long-range magnetic order, stable up to at least 19 and 26 GPa, respectively. This long-range magnetic order, which is characteristic of Sm^{3+}, appears already for a Sm valence near 2.7. In contrast to these compounds, metallic Sm, which is trivalent at ambient pressure, undergoes a series of pressure induced structural phase transitions which are associated with a progressive decrease of the ordered 4f moment.

1. Introduction

Considerable interest has been aroused in the past few decades in the study of intermetallic compounds based on anomalous lanthanides (Ce, Yb, Tm, Eu and Sm) because of the rich variety of properties that they have (intermediate valence, heavy fermion behaviour, . . .). More recently, particular attention was focused on 4f intermetallics which are close to a magnetic instability, because of the observation of unconventional superconductivity in the vicinity of a quantum critical point (QCP), where the magnetic order is destroyed [1]. In the specific case of Sm, the competition between the two possible valence states, nonmagnetic Sm^{2+} with a $4f^6$:$^7F_0$ configuration and magnetic Sm^{3+} with a $4f^5$:$^6H_{5/2}$ configuration, can sometimes lead to the formation of an intermediate valence ground state which shows peculiar electronic and

magnetic properties [2]. The charge state can be eventually tuned towards integer trivalency by the application of external pressure, with the consequent onset of long-range magnetic order owing to the fact that Sm^{3+} is a Kramers ion. Well-known examples of intermediate valence Sm compounds are the high pressure 'golden' phases of the Sm monochalcogenides (SmS, SmSe and SmTe) [3] and SmB_6 [4]. They belong to the class of Kondo insulators or narrow-gap semiconductors, which behave at high temperature like an array of independent localized moments interacting with itinerant conduction electrons, whereas at low temperature they develop clear narrow-gap properties.

At ambient pressure SmS is a nonmagnetic semiconductor (black phase), with nearly divalent Sm ions, crystallizing in the NaCl-type structure. At a very low pressure $p_{B-G} \sim$ 0.65 GPa at room temperature, it undergoes an isostructural first-order phase transition to an intermediate valence metallic state (golden phase), with a large volume collapse ($\sim 8\%$) and a valence $v \approx 2.6$ just above p_{B-G} [2]. The temperature dependence of the electrical resistivity shows the opening of a small gap at low temperatures for pressures between p_{B-G} and $p_\Delta = 2$ GPa. The gap closes continuously as pressure is increased and disappears for $p > p_\Delta$, leaving the system in a metallic ground state [5, 6]. In the golden phase the valence increases continuously with pressure, with an inflection point at p_Δ ($v \sim 2.7$) [7], and the trivalent state is reached only at considerably higher pressure ($p_{3+} > 10$ GPa) [7, 8]. Recently a first-order transition at p_Δ with the appearance of long-range magnetic order associated with intermediate valence has been evidenced by nuclear forward scattering (NFS) of synchrotron radiation [9] and specific heat [10]. The magnetically ordered state behaves like that of a stable trivalent compound, with values of the hyperfine parameters as expected for a Γ_8 ground state (produced by the action of a cubic crystal field on the Sm^{3+} ions) and almost independent of pressure in the range 2–19 GPa, while the ordering temperature T_m increases smoothly from 15 K at p_Δ to 24 K at 8 GPa. Considerable short-range magnetic correlations develop above T_m and persist up to about $2T_m$.

Analogously to golden SmS, SmB_6 is an intermediate valence ($v = 2.6$ at ambient pressure and room temperature) insulator [2]. However, at temperatures above ~ 70 K the electrical resistivity and the Hall effect are rather typical of a bad metal, and only for $T < 70$ K does the conductivity start to decrease with temperature by several orders of magnitude (two to five, depending on the quality of the sample) because of the opening of an insulating gap of the order of 10–20 meV [11, 12]. Despite the intermediate valence ground state of SmB_6, the form factor as determined by means of neutron scattering is that expected for Sm^{2+} [13], as already observed for similar systems such as golden SmS and TmSe [14]. However, the magnetic excitation spectrum shows that the 'true' ground state of SmB_6 is an unusual quantum mechanical superposition of a divalent component of $4f^6$ configuration with a $4f^5 5d$ loosely bound state, where a 4f electron is only partially delocalized and free to move within a limited volume [15–17]. Although this ground state is nonmagnetic, ^{11}B NMR measurements have evidenced the onset of dynamical magnetic correlations below ~ 15 K [18]. When external pressure is applied, the semiconducting gap decreases and finally closes at a critical pressure $p_\Delta \approx 4$–7 GPa, above which the system behaves as a metal at all temperatures [19–22]. At p_Δ the resistivity has a less than quadratic dependence on temperature down to 1.5 K, suggesting that a QCP is crossed when the gap closes [22]. The valence has been shown to increase smoothly from 2.6 at ambient pressure to 2.8 at 10 GPa, with an inflection point at ~ 5.5 GPa at the gap closure [23, 24], in analogy with SmS at 2 GPa.

In contrast to SmS and SmB_6, metallic Sm is at ambient pressure in a trivalent state with long-range antiferromagnetic order below ~ 106 K. However, recent theoretical calculations predict that the 4f electrons should become completely delocalized with a volume contraction corresponding to a pressure of the order of ~ 100 GPa [25], which can be achieved with

the diamond anvil cell (DAC) technique. Sm crystallizes at ambient pressure in the Sm-type structure, with a unit cell consisting of the periodic stacking of nine hexagonal planes ($A_cB_hA_hB_cC_hB_hC_cA_hC_h \ldots$) [26]. The sublattice formed by the six planes with a hexagonal nearest neighbour environment (indicated by the subscript h) orders antiferromagnetically at $T_{Nh} = 106$ K, while the planes with approximately cubic local symmetry (indicated by the subscript c) order independently only below $T_{Nc} = 14$ K [27, 28]. The 4f ordered magnetic moment is ∼0.6 μ_B [28], lower than the free ion value of 0.71 μ_B for the Sm^{3+} ion. High pressure resistivity studies performed up to 43 GPa show that, in the range between ambient pressure and 6 GPa, T_{Nh} decreases while T_{Nc} increases with pressure [29]. Above 6 GPa the two Néel transitions occur at the same temperature, increasing with pressure and reaching ∼135 K at 43 GPa. At higher pressure, only structural investigations have been performed, showing the presence of five successive structural phase transitions between ambient pressure and 189 GPa [30, 31]. In particular, above 91 GPa Sm adopts a body-centred tetragonal structure, in which calculations show that the 4f electrons are delocalized and that Sm is an itinerant magnet with spin moment of ⩾4 μ_B [25]. This moment is very sensitive to pressure and disappears when the volume is sufficiently reduced.

In this paper we present further results on golden SmS (a detailed discussion of previous recent results is given in [9, 10]) and new results on SmB_6 and metallic Sm at high pressures. These results were obtained by combining [149]Sm nuclear forward scattering (NFS) of synchrotron radiation with high pressure specific heat measurements (for a recent review on NFS see [32]). From the NFS data we obtained information about the magnetic hyperfine field at the [149]Sm nuclei as a function of pressure and temperature, and from the combination of NFS and specific heat we were able to determine the ordering temperature T_m of the Sm atoms and its pressure dependence. In particular we have obtained clear evidence that SmB_6, analogously with golden SmS, develops long-range magnetic order at pressures above p_Δ. These magnetically ordered states are stable up to at least 19 and 26 GPa for SmS and SmB_6, respectively. Moreover, in the low pressure intermediate valence state of both compounds (and down to ambient pressure for SmB_6), short-range magnetic correlations are present at low temperatures. In the case of metallic Sm, the magnetic hyperfine field decreases monotonically with pressure and is reduced by almost 40% at 46 GPa with respect to ambient pressure.

2. Experimental methods

The SmS sample was prepared as described in [9]. Samarium hexaboride single crystals were grown by a standard aluminium flux technique [33, 34]. SmB_6 powder was pre-synthesized by reacting boron on samarium oxide (borothermal reduction) under high vacuum using RF heating. The quality of the sample was checked by means of x-ray powder diffraction and showed the presence of pure SmB_6 with no trace of parasitic phases. For both SmS and SmB_6 the [149]Sm NFS measurements were performed on powders made with isotopically enriched (to 97%) Sm, while the specific heat measurements were performed on single crystals made with natural Sm. The metallic Sm sample was a polycrystalline foil, isotopically enriched to 97% in [149]Sm, commercially available from Oak Ridge National Laboratories.

High pressure was applied to the samples using the diamond anvil cell technique, with argon or nitrogen used as the pressure transmitting medium. The pressure was measured and changed always at room temperature for the NFS measurements, whereas it was measured and changed *in situ* using the set-up described in [35] for the specific heat measurements performed at CEA Grenoble. The [149]Sm NFS measurements (resonant energy $E_0 = 22.494$ keV; 5/2–7/2 transition) were performed at the undulator beamline ID22N [36] of the European Synchrotron Radiation Facility, Grenoble, France, and a more detailed description of the experimental set-up is given in [9]. NFS is a technique related to the Mössbauer effect; thus similar microscopic
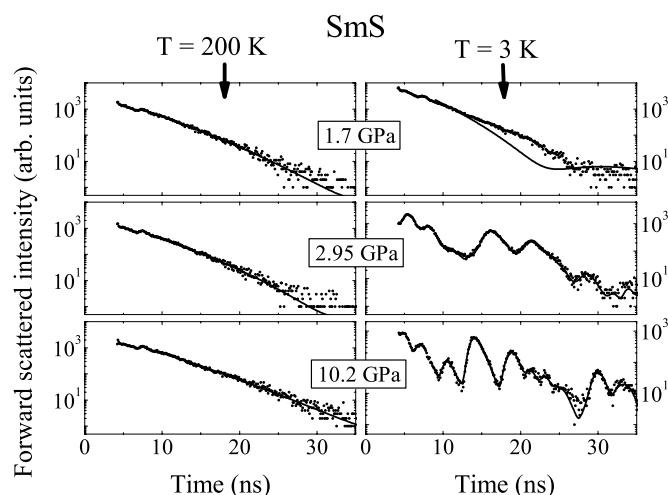
Figure 1. ^{149}Sm NFS spectra of SmS at $T = 200$ and 3 K for some selected pressures. The dots represent experimental data points, while the curves are fits.

Figure 2. ^{149}Sm NFS spectra of SmB$_6$ at $T = 200$ and 3 K for some selected pressures. The dots represent experimental data points, while the curves are fits.
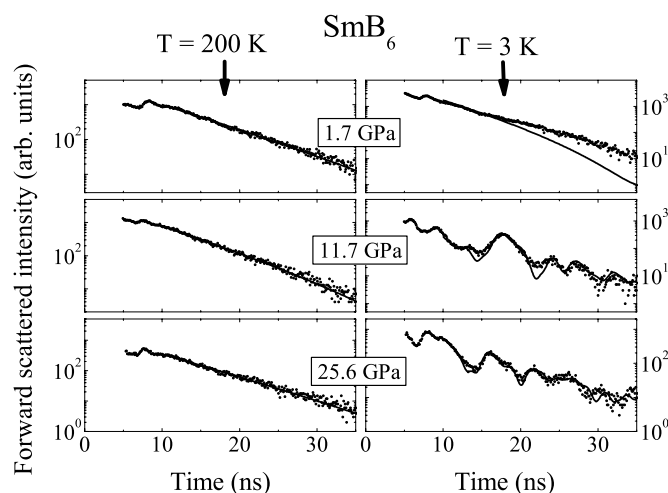
information to that inferred from conventional Mössbauer spectroscopy can be obtained. This allows one to determine the pressure dependence of the magnetic hyperfine field B_{hf}, of the ordering temperature T_m and of the electric field gradient (EFG) V_{zz} at the ^{149}Sm nuclei. The change of the 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.

3. Pressure induced magnetic order in SmS and SmB$_6$

3.1. Long-range magnetic order

3.1.1. Ground state properties as seen by means of NFS. Figures 1 and 2 show typical NFS spectra recorded at various temperatures and pressures for golden SmS and SmB$_6$, respectively. At high temperatures (left panel in the two figures) and for all pressures the spectra are characteristic of unsplit nuclear levels, as expected for Sm ions in the absence of magnetic order and in an environment of cubic symmetry (NaCl-type structure for SmS and CsCl-type structure for SmB$_6$). A clear quantum beat pattern, due to the combined

action of magnetic dipole and electric quadrupole interactions on the nuclear levels of ^{149}Sm, appears at low temperatures (right panel of the two figures, $T = 3$ K) for pressures higher than $p_{\text{c,SmS}} \approx 2$ GPa for SmS and $p_{\text{c,SmB}_6} \approx 9$ GPa for SmB$_6$. This is a clear indication that magnetic order sets in in both compounds at high pressure and low temperature. The analysis of the spectra, performed with the software MOTIF [37, 38] using the full dynamical theory of nuclear resonance scattering, including the diagonalization of the complete hyperfine Hamiltonian, reveals that for SmS at 2.35 GPa and 3 K only a fraction (corresponding to ~72%) of the Sm atoms show magnetic order, the rest being paramagnetic. However, the fraction increases rapidly with pressure and reaches 100% above ~3 GPa. At 2.35 GPa we deduce values of 261(10) T and $-1.50(6)$ mm s^{-1} for the magnetic hyperfine field B_{hf} and the induced quadrupole interaction ΔE_{Q}, respectively [9]. For SmB$_6$ at 9.7 GPa and 3 K the analysis reveals that all Sm ions are magnetically ordered. The saturation values of the hyperfine parameters at this pressure and 3 K are $B_{\text{hf}} = 246(20)$ T and $\Delta E_{\text{Q}} = -1.27(12)$ mm s^{-1}. In the vicinity of the critical pressures $p_{\text{c,SmS}}$ and $p_{\text{c,SmB}_6}$ the low temperature NFS spectra cannot be accounted for by a single set of hyperfine parameters, but broad distributions of both B_{hf} and ΔE_{Q} are present at the ^{149}Sm nuclei, larger in SmB$_6$ than in SmS. The average values of the hyperfine parameters are considerably reduced with respect to the free ion values for Sm^{3+} ($B_{\text{hf}} = 338$ T and $\Delta E_{\text{Q}} = -2.1$ mm s^{-1} [39]). This can be ascribed to the effect of the cubic crystal field acting on the Sm^{3+} ions: the lowest multiplet ^{6}H$_{5/2}$ is split into a Γ_7 doublet and a Γ_8 quartet (here and in the following we will neglect the possible mixing of the ground multiplet with excited multiplets through exchange interactions), associated with completely different values of the hyperfine parameters ($B_{\text{hf}} = 113$ T and $\Delta E_{\text{Q}} = 0$ for Γ_7, while $B_{\text{hf}} = 250$ T and $\Delta E_{\text{Q}} = -1.7$ mm s^{-1} for Γ_8). Our measured values for both compounds, especially those for the magnetic hyperfine field, compare well with those calculated for a Γ_8 state. However, one must keep in mind that, at least for the lowest pressures above $p_{\text{c,SmS}}$ and $p_{\text{c,SmB}_6}$, the magnetic order coexists with intermediate valence and therefore the ground state wavefunction can be considerably more complicated than the simple one describing the Γ_8 quartet. For both compounds the hyperfine parameters in the magnetically ordered state have only a very weak dependence upon pressure in the range studied, showing however a slight continuous increase of magnitude as pressure increases. At the same time, the widths of the distributions of B_{hf} and ΔE_{Q} decrease with increasing pressure but remain finite even at the highest pressures (the distribution of B_{hf} has a relative width of ~3% at $p > 5$ GPa for SmS and of ~7% at $p > 11$ GPa for SmB$_6$). These facts prove that the pressure induced magnetic order in these two compounds is very stable and that the transition into the trivalent state (which occurs for $p > 10$–12 GPa in the case of SmS [8]) is not associated with any anomaly in the pressure dependence of the hyperfine parameters. This fact and the good agreement between the measured values of B_{hf} and ΔE_{Q} and those expected for Sm^{3+} ions in a cubic crystal field might be an indication of the fact that, in the high pressure metallic state, these two compounds behave like stable trivalent compounds, independently of υ and similarly to TmSe above 3 GPa [40].

3.1.2. Temperature dependence: NFS and specific heat. In order to shed more light on the properties of the high pressure magnetically ordered state, we have performed temperature dependent NFS and specific heat measurements at various pressures. The temperature and pressure dependences of the specific heat for golden SmS and SmB$_6$ are shown in figures 3(a) and (b), respectively. The presence of sharp anomalies at temperatures $T_{\text{m}}(p)$ for pressures higher than 2 GPa for SmS and ~9 GPa for SmB$_6$ is a clear indication that the order observed by NFS in both systems at high pressure is long-range magnetic order. T_{m} is found to increase from 15 K at 2 GPa to 24 K at 8 GPa in SmS, whereas it has a value of ~12 K, independent
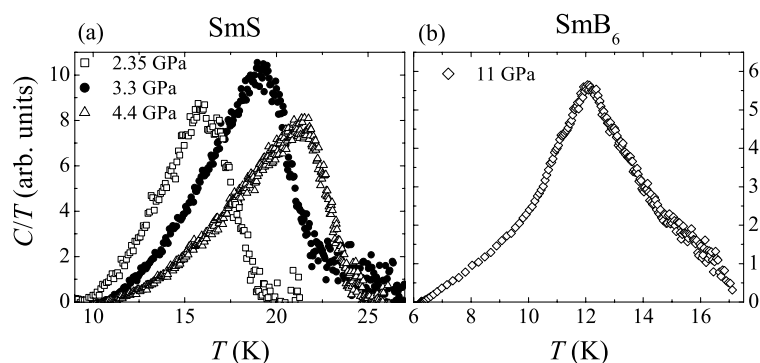
Figure 3. The specific heat of (a) SmS and (b) SmB$_6$ as a function of temperature and pressure.

of pressure up to 16 GPa, in SmB$_6$. The temperature dependence of the NFS spectra of SmS for $p > 2$ GPa does not reveal any sharp transition at T_m as regards the values of B_{hf} (see figure 4) and ΔE_Q, but a continuous decrease with increasing temperature up to $\sim 2T_m$, where they become zero. The presence of hyperfine interactions at temperatures higher than T_m can be seen as due to the persistence of short-range magnetic correlations (probably of dynamical nature) in the paramagnetic phase. However, an anomaly in the temperature dependence of the NFS count rate (which is a complicated function of the physical properties of the compound under study) is clearly visible (see figure 5), with a minimum in the vicinity of T_m and the following steep increase upon entrance into the paramagnetic state. A similar behaviour is found in SmB$_6$, with a minimum in the count rate at the value of T_m determined by the specific heat measurements and the subsequent increase as temperature increases, as shown in figure 5. However, in this case a clear transition from the long-range magnetic order below T_m to a phase characterized by short-range magnetic correlations is directly observed in the NFS spectra, as shown in figure 4: above T_m the average values of B_{hf} and ΔE_Q are considerably reduced, their distribution is much broader and finally only a fraction of the Sm ions feel these interactions, which slowly decrease and disappear at temperatures higher than ~ 50 K for all pressures up to 26 GPa.

3.2. Short-range magnetic correlations

In the top panels of figures 1 and 2 spectra are shown which are characteristic of the low pressure ($p = 1.7$ GPa) semiconducting intermediate valence states of golden SmS and SmB$_6$, respectively. At 3 K, the NFS spectra cannot be analysed properly if the assumption is made that the nuclear levels are not split by any hyperfine interaction, as would be expected for a nonmagnetic ground state: this is clear from the fact that the best fit (shown in the figures as a curve) to the two NFS spectra at 3 K and 1.7 GPa simply does not reproduce the measured data. The only reasonable agreement between calculated and experimental curves can be obtained in the hypothesis that at least a fraction of the Sm ions feel hyperfine interactions due to the presence of (short-range) magnetic correlations, which can be seen as a precursor of the incipient onset of long-range magnetic order above $p_{c,SmS}$ or p_{c,SmB_6}. Because of the extremely broad distributions of these hyperfine interactions, they do not show up as a clear beat pattern in the NFS spectra but rather only as a slowing down of the nuclear decay and this prevents a precise analysis of their strength. The broad maxima present in the temperature dependence of the specific heat for pressures $1.3 < p < 2$ GPa in the case of SmS and $7 < p < 9$ GPa for SmB$_6$ can also be interpreted in the framework of the onset of low temperature short-range
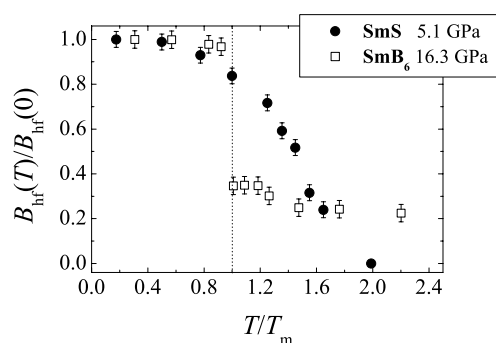
Figure 4. The reduced magnetic hyperfine field of SmS (as an example at 5.1 GPa) and SmB_6 (as an example at 16.3 GPa) as a function of the reduced temperature. T_m is the temperature for the onset of long-range magnetic order as determined from the specific heat.
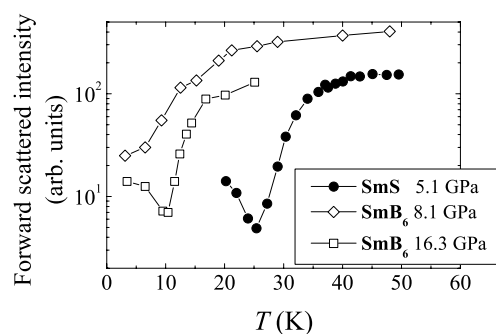

Figure 5. The NFS intensity for SmS (as an example at 5.1 GPa) and SmB_6 (as an example at 8.1 and 16.3 GPa) as a function of temperature.

slow magnetic correlations for pressures just below $p_{c,SmS}$ and p_{c,SmB_6}. Although the NFS spectra of SmB_6 are characterized by the presence of short-range correlations even at ambient pressure, appearing always below 50–100 K independently of pressure, two regimes can be distinguished in the temperature dependence of the NFS count rate: for $0 \leqslant p \leqslant 5$ GPa there is no appreciable variation between 3 and 300 K, whereas for $5 \leqslant p \leqslant 9$ GPa a steep increase is observed between ∼10 and ∼50 K, similar to the one observed for higher pressures, but no minimum is present (see figure 5). The interval between 5 and 9 GPa, approximately where the semiconducting gap closes, can therefore be seen as a region of transition between the low pressure gapped state and the high pressure state with long-range magnetic order.

The ground state of intermediate valence golden SmS and of ambient pressure SmB_6 is generally considered as a nonmagnetic state: the magnetic susceptibility does not show any paramagnetic Curie–Weiss divergence at low temperatures, as would be expected for Sm^{3+} ions, and neutron diffraction experiments do not show any trace of magnetic correlations. However, strong Sm^{2+}–Sm^{2+} (ferromagnetic) exchange interactions being present already in the nearly divalent black phase of SmS has been demonstrated by ESR measurements [41] and an anomalous temperature dependence of the ^{11}B relaxation rate in NMR experiments below 15 K points towards the presence of magnetic correlations in SmB_6 at ambient pressure too [18]. Our studies therefore seem to confirm the presence of slowly fluctuating moments in the semiconducting phase of SmB_6. Owing to the divalent-like character of the ground state wavefunction of SmB_6, the exchange interactions mentioned above can induce a strong mixing of the nonmagnetic ground multiplet $^7F_0$ of divalent Sm with its magnetic first excited multiplet $^7F_1$, which lies only ∼36 meV (∼420 K) higher in energy. Moreover, the magnetic excitation spectrum of SmB_6, as measured by means of inelastic neutron scattering [15, 16], shows the presence below ∼50–100 K of a sharp transition at only 14 meV (∼160 K), which is interpreted as an excitation from the 'true' intermediate valence ground state ($J = 0$) into
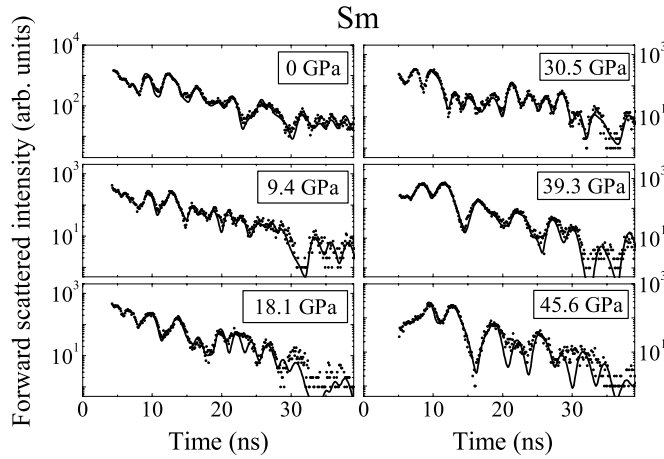
Figure 6. ^{149}Sm NFS spectra of metallic Sm at $T = 3$ K for some selected pressures. The dots represent experimental data points, while the lines are fits.

its first excited state ($J = 1$). In this temperature range the J mixing could therefore even be much stronger than expected for the free Sm^{2+} ion, thus making the appearance of short-range magnetic correlations possible.

Recently a simple expression has been proposed [42, 43] for the extension to a lattice of the Kondo temperature (T_K) formula for a single Ce impurity ($T_K = (1 - n_f)\Delta$, with n_f and Δ the occupation number of the lower valence configuration (trivalent for Ce and divalent for Sm and Yb) and the width of the virtual bound state, respectively). For a lattice, Δ can be replaced by the Fermi temperature ($T_F = (1 - n_f)^{2/3}D_0$). In the case of Sm (where the equilibrium of the valence is given by the expression Sm$^{2+} \leftrightarrow$ Sm^{3+} + 5d and the valence can be expressed as $v = 3 - n_f$), this gives $T_{KL} = n_f(1 - n_f)^{2/3}$; this implies that T_{KL} will reach a maximum as n_f goes from 0 to 1 (whereas it increases continuously in the case of Ce). When $k_B T_{KL}$ becomes lower than the crystal field splitting, slow relaxation processes are expected and thus magnetic ordering occurs.

4. The effect of pressure on metallic Sm

NFS measurements of metallic samarium have been performed at temperatures between 3 and 300 K in the pressure range 0–46 GPa, spanning over five different crystallographic structures. Typical measured spectra are shown in figure 6, while the pressure dependence of the saturation ($T = 3$ K) hyperfine parameters is shown in figure 7.

4.1. Magnetic properties at ambient pressure

At ambient pressure, in the Sm-type structure, two inequivalent Sm sites with hexagonal or cubic coordination are present, in a ratio of 2:1, respectively. At high temperatures, above $T_{Nh} = 106$ K, both sites are expected to show an electric quadrupole interaction due to the non-cubic environment of all Sm atoms, owing to the fact that the ratio c/a of the lattice parameters is smaller than its ideal value for the Sm-type structure. By comparison with the measured values of the electric field gradients in dhcp La metal [44], one can roughly estimate the lattice contribution to the electric quadrupole interaction of both sites in Sm metal to be very small, of the order of only ∼+0.15 mm s^{-1}. Although the NFS spectra are not very well resolved at high temperatures, the best fit to the data gives $\Delta E_Q^h = 0.0(1)$ mm s^{-1} for the hexagonal sites and $\Delta E_Q^c = +0.2(1)$ mm s^{-1} for the cubic sites at $T = 200$ K. At low temperatures, below $T_{Nc} = 14$ K, both sites are expected to show a combination of magnetic hyperfine and electric
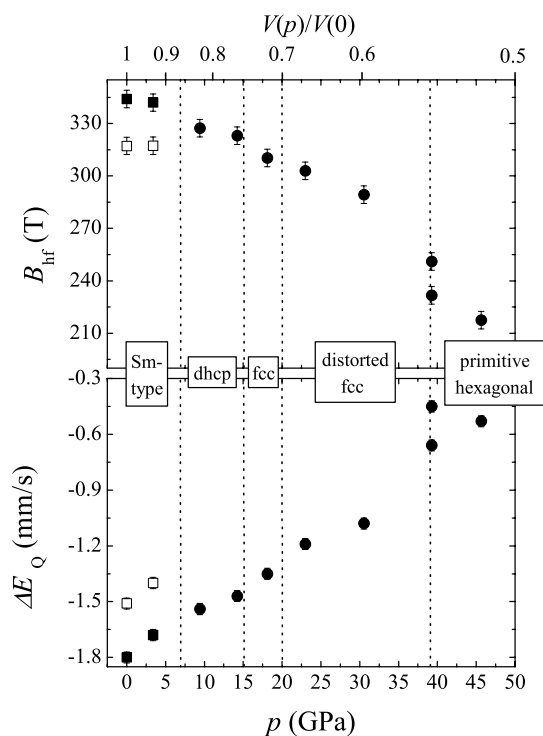
Figure 7. The dependence on pressure and reduced volume of the magnetic hyperfine field B_{hf} and of the electric quadrupole interaction ΔE_Q of Sm metal at $T = 3$ K. The symbols ■ and □ refer to the hexagonal and cubic sites of the Sm-type structure, respectively, while ● symbols refer to the single site for the other structural phases. The reduced volume scale is determined approximately from [31]. Note the coexistence of the distorted fcc and primitive hexagonal phases at 39 GPa.

quadrupole interactions. Here $|\Delta E_Q|$ should be considerably enhanced with respect to its high temperature value, because a dominant 4f term adds to the lattice contribution (which usually has only a slight dependence on temperature). The analysis of the NFS spectra reveals that the magnetic hyperfine field for the hexagonal sites at $p = 0$ and $T = 3$ K, $B_{hf}^h = 344(5)$ T, is very close to the value expected for a free Sm^{3+} ion (338(6) T [39]), and it compares well with the average value found at 4.2 K by Mössbauer spectroscopy (345(18) T) [45]. However, the electric quadrupole interaction $\Delta E_Q^h = -1.80(3)$ mm s^{-1} is considerably reduced with respect to the free ion value of -2.1 mm s^{-1} [39] and the lattice contribution alone cannot account for the difference. Moon and Koehler [28] have calculated approximate ground state wavefunctions for the cubic and hexagonal sites of Sm taking into account the crystal field and exchange interactions, in order to explain their measured neutron scattering amplitudes. For the hexagonal sites, in particular, their calculations reveal that the relatively strong exchange interactions, responsible for the high Néel temperature of 106 K, induce a mixing of the $J = 5/2$ ground state with the $J = 7/2$ excited state, with a reduction of the 4f magnetic moment of these sites (0.56 μ_B) with respect to the Sm^{3+} free ion value (0.71 μ_B). Using the same wavefunction, we have calculated the expected values of the magnetic hyperfine field and of the electric quadrupole interaction for this ground state, which amount to $\sim$350 T and ~ -1.8 mm s^{-1} and are therefore in good agreement with our measured values. This is therefore one example of the complicated relationship between magnetic moment and hyperfine magnetic field which is quite typical for Sm compounds, where the mixing of multiplets with

different J can at the same time induce a reduction of the magnetic moment as compared to the free ion value and an increase of the magnetic hyperfine field.

At the cubic sites, the analysis of the NFS spectra indicates that the hyperfine parameters are considerably reduced with respect to those of the hexagonal sites: $B_{hf}^c = 317(5)$ T and $\Delta E_Q^c = -1.51(3)$ mm s^{-1}, and even if the larger lattice contribution to the electric field gradient at the cubic sites (as determined at high temperature) is considered, the difference remains. A possible explanation for this can be given if one interprets the fact that the ordering temperature of the cubic sites ($T_{Nc} = 14$ K) is far lower than that of the hexagonal sites ($T_{Nh} = 106$ K) as a consequence of the reduced strength of the exchange interactions at the cubic sites, which can be reflected in a lower degree of mixing of the $J = 7/2$ excited multiplet into the ground one. The calculation of Moon and Koehler [28] shows indeed that the ground state wavefunction of the cubic sites does not contain any mixing with the $J = 7/2$ multiplet at all and that a larger 4f magnetic moment is expected for these sites. By using the wavefunction which best fits their neutron data, we obtain values of $\sim$270 T for the magnetic hyperfine field and ~ -1.5 mm s^{-1} for the 4f contribution to the electric quadrupole interaction. Although these values are lower than our measured ones, they qualitatively confirm that a reduction of the exchange interaction is in this case reflected in a decrease of the values of both magnetic hyperfine field and electric quadrupole interaction. We think that our set of data (including the complete temperature dependence of B_{hf} and ΔE_Q) in combination with the neutron data of Koehler and Moon [27] might help in evaluating better the effect of crystal field and exchange interactions on the ground state properties and especially on the value of the ordered magnetic moment of metallic Sm at ambient pressure, which is still a subject of controversy [46].

4.2. Magnetic moment decrease at high pressure

As pressure increases, the Sm-type structure is expected to be stable up to $p \sim 7$ GPa at 4.2 K. At $p = 3.4$ GPa we indeed still observe the presence of hexagonal and cubic sites in the ratio 2:1, with different hyperfine interactions, but in both cases slightly reduced with respect to the ambient pressure values. Starting from $p = 9.4$ GPa, in correspondence with the transition to the dhcp phase (La-type structure, stable up to $\sim$15 GPa at 4.2 K), the NFS spectra can be properly analysed with a single set of hyperfine parameters at $T = 3$ K. Although in this structure two different crystallographic sites still exist for Sm, with hexagonal and cubic coordination, respectively, and in the ratio 1:1, they seem therefore to be characterized by the same values of their hyperfine parameters. This is in agreement with the resistivity studies of [29], where only one magnetic phase transition is observed for $p > 6$ GPa. The dhcp structure of Sm metal can be stabilized at ambient pressure, if samples are produced in the form of thick films on appropriate substrates. Studies of these films with resonant magnetic x-ray scattering and neutron scattering [47] reveal that, despite the presence of two crystallographically inequivalent sites, Sm still orders antiferromagnetically, as in the Sm-type structure, but only one ordering temperature ($T_N = 25$ K) is observed for both hexagonal and cubic sites, owing probably to the enhanced coupling of layers with different coordinations and the consequent increase of the mutual exchange. Our results are in perfect agreement with these findings, and the hyperfine interactions that we determine from our measurements at 9.4 GPa have a value intermediate between those of the two sites in the Sm-type phase (see figure 7).

When pressure is increased further, the successive structural transitions from dhcp to fcc, from fcc to distorted fcc and from distorted fcc to primitive hexagonal are crossed at 15, 20 and 39 GPa, respectively [31]. At 39 GPa the coexistence of the two phases is responsible for the presence of two sets of hyperfine parameters as shown in figure 7; however, at 46 GPa the pure primitive hexagonal phase is observed. From figure 7 it is evident that at 3 K the strengths

of both the magnetic hyperfine field and electric quadrupole interaction decrease considerably in the pressure range between 0 and 46 GPa, reaching the values of $B_{hf} = 218(5)$ T and $\Delta E_Q = -0.53(3)$ mm s^{-1} at the highest pressure, corresponding to relative reductions of $\sim 40\%$ and $\sim 70\%$ with respect to the ambient pressure values, respectively. In the same pressure interval, the volume of the unit cell shrinks by almost 50% [31]. The large reduction of the magnetic hyperfine field is due to the variation with pressure of its different components. The largest contribution to the measured value is due to the 4f electrons and is directly related to their magnetic moment, but other contributions arise from the polarization of core electrons and of conduction electrons. In Sm compounds the core polarization has the same sign as the 4f contribution but a considerably smaller value (that can be estimated to amount to ~ 15 T), and it is generally considered as not dependent on pressure [48]. The conduction electron polarization can, on the other hand, give a large contribution to the hyperfine field, with possibly also a large pressure dependence. At the present stage it is therefore not possible to state clearly whether the strong reduction of B_{hf} is due to a corresponding reduction of the 4f magnetic moment or to a simple change in the balance between the 4f and the conduction electron contributions. However, the decrease of B_{hf} is associated with an even larger decrease of the electric quadrupole interaction ΔE_Q, which cannot be explained by the variation of its lattice component alone. We therefore believe that the large decrease of both B_{hf} and ΔE_Q at the same time can be taken as an indication that the 4f magnetic moment of Sm is reduced by pressure. Moreover, although the decrease of the hyperfine parameters is mostly continuous, the entrance into the primitive hexagonal high pressure phase at 39 GPa seems to be accompanied by a small discontinuity (downwards) of both B_{hf} and ΔE_Q, which can be interpreted as a further sign of the incipient delocalization of the 4f electrons, which are proposed to be involved in the chemical bonding in this phase [31].

5. Conclusions

In conclusion, we have studied the effect of external pressure on the magnetic and electronic properties of several Sm compounds, which are nearly divalent (SmS), intermediate valent (SmB$_6$) or trivalent (Sm metal) at ambient pressure. In both SmS and SmB$_6$, where the valence is known to increase smoothly with pressure, we observe the onset of long-range magnetic order at a critical pressure which corresponds approximately to the entrance of these systems into the metallic state. The ordered state is very stable towards pressure and has the properties expected for trivalent compounds, although both systems are still intermediate valent when the magnetic order appears. For pressures just below that for the onset of long-range order we observe the presence at low temperatures of short-range magnetic correlations of dynamical origin. These correlations are found to persist in SmB$_6$ even at ambient pressure. In the case of metallic Sm, pressure induces a strong decrease of the magnetic hyperfine field and the electric quadrupole interaction at the ^{149}Sm nuclei. This can be related to a smooth decrease of the Sm 4f moments when pressure increases. The small discontinuity in the pressure dependence of the hyperfine field when Sm undergoes the transition into the primitive hexagonal phase at 39 GPa might indicate the onset of the delocalization of the 4f electrons. However, further studies are necessary at higher pressures in order to obtain the full delocalization.

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