

Local-moment collapse in compressed samarium metal

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We present theoretical evidence that the recently observed ultra-high-pressure phase in samarium metal is a delocalized $4f$ -electron system with an itinerant spin moment of $\sim 4\mu_B$. By comparing the total energy (at $T=0$) of the localized fcc phase and the delocalized bct phase we conclude that Sm metal will undergo a delocalization of the $4f$ shell in the Mbar pressure range. This is consistent with the previous experimental observation of an fcc \rightarrow bct transition at ~ 1 Mbar. Furthermore, our calculations show that the correct crystal structure (bct) is obtained only for delocalized $4f$ states, and the calculated c/a ratio (1.70) compares well with experimental data (1.76).

Recent developments of experimental high-pressure techniques have made it possible to study materials at static pressures in the megabar range.¹⁻³ One can now begin to investigate solids under new experimental conditions, where the volume is reduced to typically half of its normal value ($V/V_0=0.5$, where V_0 is the equilibrium volume). It has therefore become a great challenge for theory to cover this new physical regime for various classes of materials. The magnetic rare-earth metals are especially interesting in this connection. Under normal conditions the $4f$ electrons are localized and the associated magnetic moments are very well described by atomic theory.⁴ This fact forms the basis for the so-called standard model for rare-earth systems. Furthermore, the atomic volumes and the crystal structures for the lanthanides are well understood from a trivalent picture (Ce, Eu, and Yb are exceptions) and the metallic bond originates from a rather broad band containing three s,p,d electrons. Also, all trivalent rare-earth metals crystallize in hexagonal close-packed structures (hcp, Sm-type, and dhcp). Theoretical calculations^{5,6} show that the crystal structure sequence is correlated with the d occupation of the valence band (or to a related quantity, the ratio between the metallic and ionic radii⁷). It has actually been demonstrated that the crystal structure sequence found when traversing the lanthanide series, dhcp-Sm-type-hcp, originates from the decreasing d occupation.^{5,6} Also, applying pressure to a late lanthanide metal (with lower d occupation) increases the d character of the metallic bond and correspondingly the reversed structure sequence, hcp-Sm-type-dhcp, is observed. At sufficiently high pressure the trivalent lanthanide metals transform first to the fcc structure and then to a trigonal distortion of the fcc structure,^{2,3,8} called fcc'. Hence, all previous high-pressure work show transitions between close-packed structures, and the understanding for this is based on a trivalent ground state with chemically inert $4f$

electrons.⁵⁻⁷ However, recent experimental high-pressure data² show that at ~ 1 Mbar Sm adopts a quite unique body-center tetragonal (bct) structure. These types of structures (open, low symmetric) have previously only been found in delocalized f electron metals and it is tempting to associate the bct structure with an onset of f bonding. These new and interesting data have motivated us to investigate the possibility that Sm metal becomes a delocalized f electron system at extreme compressions, using an accurate computational technique for calculating the total electronic energy at zero temperature.

In order to determine when the $4f$ states will become itinerant in Sm one has to balance the bonding energy associated with delocalized $4f$ states with the atomic polarization energy (E_{pol}) associated with localized f states. Thus, we will compare the total energy between two different electronic states for highly compressed samarium, namely, the standard localized $4f^5(^6G_{5/2})$ trivalent metallic state and the itinerant $4f$ state, where for the latter not only the s,p,d states but also the f states are part of the conduction band. The total energies for the two phases were calculated using a full potential linear muffin-tin orbital method.⁹ These calculations make no shape approximation for the charge density and potential and are based on the local density approximation of the density functional theory. The basis functions are the so-called linear muffin-tin orbitals^{10,11} and we presently use a double basis set to ensure that the expansion of the wave function is well converged. When sampling the Brillouin zone we used the special k -point method,¹² with 58–80 k points in the irreducible wedge. All states (including the core states) were treated self-consistently for both electronic configurations. For the localized phase we treated the $4f$ states as part of the core and assumed a statistical occupation of the $4f_{5/2}$ and $4f_{7/2}$ levels, which corresponds to the grand barycentre for the atomiclike $4f^5$ manifold. The total energies for the two phases will

therefore be directly comparable if the energy difference between the grand barycentre and the lowest atomic multiplet is taken into account for the trivalent state.¹³ This energy E_{pol} is known to be 5.8 eV from the analysis of atomic spectra.¹⁴ The energy E_{pol} is of course important for the calculated transition pressure (P_{tr}), and we have for that reason studied how sensitive P_{tr} is for a change in E_{pol} . In the case of samarium, where P_{tr} is relatively large, a shift of 1 eV in E_{pol} will result in a corresponding shift in the transition pressure of ~ 200 kbar. This will be discussed in more detail below, in connection to Fig. 1. We estimate the value of E_{pol} (extracted experimentally¹⁴) to be correct within a few tenths of 1 eV and therefore the accuracy of P_{tr} should be of the order of 10–50 kbar (see below).

At zero pressure the crystal structure of samarium metal is a nine-layer stacking sequence of hexagonal planes (Sm-structure) and the experimental atomic volume V_0 is equal to 33.2 \AA^3 . However, as mentioned above it is well known that the lighter lanthanides under high-pressure transform into the fcc structure.^{2,3} In the calculations for the standard local moment, trivalent samarium metal we therefore used the fcc and bcc structures (the reason for treating the bcc structure is given below). For the itinerant state we use the experimentally reported high-pressure structure, bct ($c/a = 1.76$).

Accounting for E_{pol} , we can perform a proper energy comparison between the localized and itinerant states from our calculated first principles, total energies as a function of volume.¹³ This comparison is shown in Fig. 1, where we have plotted the total energy as a function of volume both for the delocalized and localized phases.

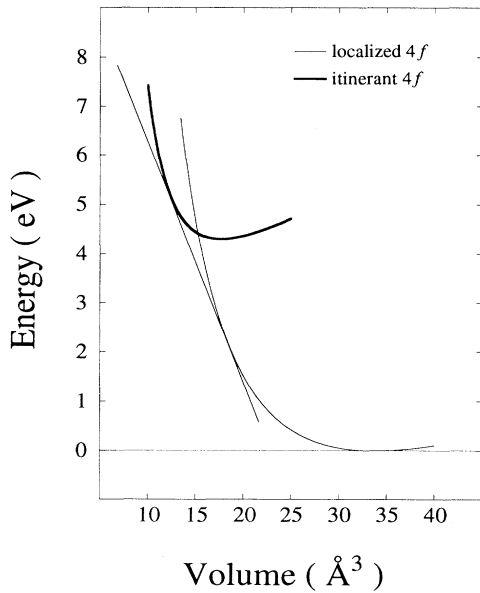


FIG. 1. Total energies for Sm with localized (thin line) and delocalized (thick line) $4f$ electrons. The energy for the localized phase is corrected to give the energy for the lowest multiplet state (see text). The transition pressure, P_{tr} , is obtained from the common tangent construction.

Notice that there is a transition from the localized fcc phase at 18.3 \AA^3 to the delocalized bct phase. The transition pressure, obtained from the common tangent shown in Fig. 1, is 0.8 Mbar. This result is consistent with the experimental finding of a bct structure being stable at high compressions since it is known that chemically bonding f electronics favor open low-symmetry structures.¹⁵ We now return to our estimate of the influence of an uncertainty of E_{pol} on the transition pressure. Shifting the localized energy curve in Fig. 1 with a few tenths of an electron volt results in a corresponding error in P_{tr} of approximately 10–50 kbar. The validity of our finding, i.e., that *the compressed phase of Sm has delocalized f states*, can be further investigated by determining crystallographic parameters, e.g., the c/a axis ratio of the bct structure. This is a very sensitive test, since crystal structure energy differences are very small and sensitive to the details of the electronic structure. We have therefore, treating the $4f$ states as delocalized, calculated the total energies of Sm using three different crystal structures; fcc, bct, and the orthorhombic α -U structure. The α -U structure was included since this structure is found in many delocalized f -electron systems [U,¹⁶ Ce,¹⁷ Pr,¹⁸ and possibly Am (Ref. 19)]. This was done at volumes where it is known experimentally that the bct structure is stable, with a c/a ratio of 1.76.^{2,3} For the α -U structure we used crystallographic parameters corresponding to α' -Ce,¹⁷ i.e., the c/a ratio was 1.97, the b/a ratio was 1.71, and the positional parameter, $2y$, was 0.23. These calculations covered the volume range $0.3 < V/V_0 < 0.4$. It was found that the bct structure is favored over the α -U structure (by ~ 4 – 8 mRy/atom) as well as over the fcc structure (by ~ 10 – 30 mRy/atom). The crystallographic energy in the α -U structure, has been shown to depend only weakly on the positional parameter $2y$ for comparable f -electron systems (uranium).²⁰ Therefore we refrained to try to optimize the crystallographic parameters c/a and b/a for this structure. We have thus compared crystal structures which are found in elements with mainly d bonding (fcc) with structures found in elements with mainly f bonding (bct and α -U) and correctly reproduced the experimentally reported structure.

To further illustrate the importance of the f electrons for dictating the correct crystal structure we have calculated the energy of the Bain path²¹ (energy as a function of the c/a ratio for the bct structure) for both delocalized and trivalent Sm at a compression $V/V_0 = 0.37$ (Fig. 2). It is worthwhile to remark here that the bct structure is the same as the bcc structure for $c/a = 1$ and the same as the fcc structure for $c/a = \sqrt{2}$. For purposes of illustration, in Fig. 2, we have normalized the total energies of the different calculations to have the same reference energy. Figure 2 shows that, for the trivalent localized $4f$ configuration, the bcc structure is stable, in disagreement with the experimental finding. However, the delocalized (paramagnetic) configuration yields the correct structure, bct. Hence, only for delocalized states can we reproduce the correct structure. However, notice in Fig. 2 that our calculated c/a ratio (1.95) is substantially larger than the experimental data (1.76). The bold line refers to a situation where the itinerant $4f$ electrons are allowed to spin

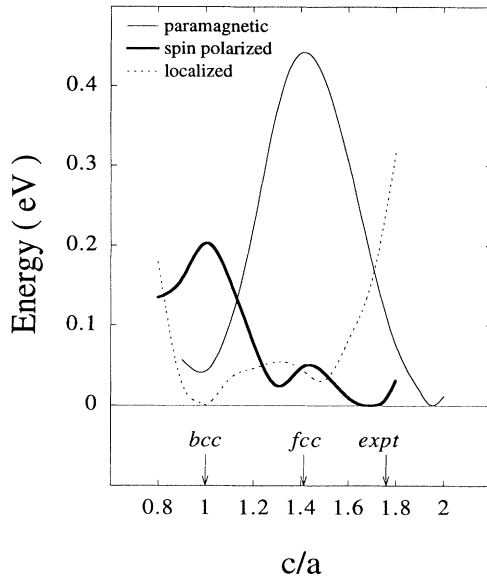


FIG. 2. Theoretical Bain path for Sm at 37% of the experimental volume. The thin solid and bold solid lines refer to a treatment of the $4f$ electrons as itinerant-paramagnetic and itinerant-ferromagnetic respectively. The dotted line represents the localized phase.

polarize (see below).

Another interesting result of these calculations is that trivalent Sm at high compressions favors the bcc structure. This is quite surprising since at pressures lower than ~ 500 kbar the trivalent lanthanide metals crystallize in fcc, hcp, dhcp, or similar hexagonally packed structures. In order to investigate this in more detail we computed the total energy of the bcc and fcc structures as a function of volume for the trivalent $4f$ localized phase (not shown). At higher volumes the fcc phase is stable but at a volume of 13.2 \AA^3 and a pressure ~ 2.7 Mbar the bcc phase becomes stable. It should be possible to stabilize this structure, at higher pressures, in similar trivalent systems as, for example, gadolinium.

As mentioned above we obtain a c/a ratio for the delocalized phase of 1.95, which is substantially larger than the experimental value of 1.76. This large disagreement indicates that the $4f$ contribution to the bonding is overemphasised. However, the calculations presented above have been subject to one restriction, i.e., we have imposed spin degeneracy. Correspondingly, this restric-

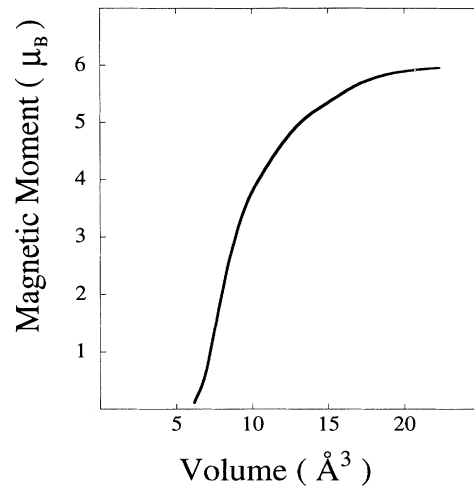


FIG. 3. The calculated spin moment for the itinerant phase of Sm as a function of volume.

tion was released and the system was allowed to break the spin degeneracy if this is energetically favorable. This is indeed the case and in Fig. 3 we display our calculated spin moment as a function of volume for the ferromagnetic state. Notice that at volumes where we find the delocalized phase to be stable (see Fig. 1) the magnetic moment is changing quite dramatically as a function of volume. Nevertheless, at the transition volume the spin moment is substantial, $\sim 4\text{--}5.5\mu_B$. At sufficiently low volumes the moment disappears and Sm metal is here a $4f$ delocalized paramagnet. We have also calculated the energy of the Bain path for the spin polarized phase of Sm (Fig. 2). Notice that, for the spin polarized state, the theoretical c/a ratio (1.70) agrees very well with experimental data. Therefore, both direct total energy considerations as well as the more indirect details of the atomic structure arrangement suggest that *Sm metal at high pressures is a $4f$ delocalized magnet*.

In conclusion, based on comparisons with experimental data, we have found strong theoretical evidence that the $4f$ moment in samarium metal has become itinerant in the Mbar pressure range. This is remarkable since the samarium $4f^5$ moment is normally considered to be extremely stable against external influences. This finding opens the prospects that even the local moments in europium, gadolinium, and terbium might become unstable at pressures attainable at laboratory conditions.

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