

Temperature and pressure dependencies of Sm valence in SmB 6 Kondo insulator probed by x-ray absorption spectroscopy

Emin Mijit, Fabienne Duc, Olivier Mathon, Angelika Rosa, Gaston Garbarino, Tetsuo Irifune, Daniel Braithwaite, Natalya Shitsevalova, Cornelius Strohm

To cite this version:

Emin Mijit, Fabienne Duc, Olivier Mathon, Angelika Rosa, Gaston Garbarino, et al.. Temperature and pressure dependencies of Sm valence in SmB 6 Kondo insulator probed by x-ray absorption spectroscopy. Physica B: Condensed Matter, 2024, 8 (28), pp.416174. 10.1016/j.physb.2024.416174. hal-04606091

HAL Id: hal-04606091 <https://hal.science/hal-04606091v1>

Submitted on 10 Jun 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Temperature and pressure dependencies of Sm valence in SmB⁶ Kondo insulator probed by x-ray absorption spectroscopy

Emin Mijit^a, Fabienne Duc^a, Olivier Mathon^b, Angelika D. Rosa^b, Gaston Garbarino^b, Tetsuo Irifune^c, Daniel Braithwaite^d, Natalya Shitsevalova^e, Cornelius Strohm⁴

^aLaboratoire National des Champs Magnétiques Intenses, CNRS-INSA-UGA-UPS, F-31400 Toulouse, France

 b European Synchrotron Radiation Facility, B.P. 220, 38043 Grenoble, France

^cGeodynamics Research Center, Ehime University, Matsuyama 790-8577, Japan

 d Université Grenoble Alpes, CEA, Grenoble INP, IRIG, PHELIQS, 38000 Grenoble, France

^e Institute for Problems of Materials Science, National Academy of Sciences of Ukraine, Krzhyzhanovsky 3, 036 80 Kiev, Ukraine

^fDeutsches Elektronen Synchrotron, Notkestrasse 85, 22607, Hamburg, Germany

Abstract

Pressure and temperature induced valence changes in the Kondo insulator SmB_6 have been investigated using x-ray absorption spectroscopy (XAS) along several isobaric cooling runs and one isothermal compression. The average valence of Sm at various pressure and temperature conditions is extracted from high quality XAS data by peak fitting procedures. The temperature dependence of the Sm valence at ambient pressure shows changes of slope near the known characteristic temperatures of gap formation (120 K) and the in-gap state (50 K). At higher pressures the average valence also shows similar temperature dependent trends upon cooling but the slope changes are less pronounced. This behavior is discussed in relation to the possible existence of an underlying first order valence transition and its critical end point. At constant temperature $(T = 20 \text{ K})$, the Sm valence increases rapidly with pressure; however, it remains far below the expected integer value $(3+)$ near the onset of the magnetic ordering and gap closure. In addition, the local structure of SmB_6 at ambient conditions has been analyzed using extended x-ray absorption fine structure.

Keywords: Kondo insulator, SmB_6 , valence fluctuation, x-ray absorption spectroscopy

1. I. Introduction

Strong electronic correlations in the rare-earth based f electron compounds give rise to a variety of interesting behaviours, including quantum criticality, unconventional superconductivity, heavy fermions and non-Fermi liquid states. In recent years, critical valence fluctuations and valence transitions have attracted growing attention as a key ingredient for understanding those unusual phenomena [1, 2, 3]. In many Ce and Yb-based heavy fermion compounds, optimal superconductivity or quantum critical point occurs at the pressure of a valence crossover, which arises from a virtual critical end point (CEP) of an underlying first order valence transition [1, 2, 3].

The intermediate valence compound $SmB₆$ has been extensively studied in the past as a prototypical Kondo insulator [4, 5], and experienced tremendous renewed interest in recent years for its topologically protected metallic surface state [6, 7]. At ambient temperature (T) , $SmB₆$ behaves like a correlated poor metal but undergoes a metal to insulator crossover at lower temperatures [4]. The opening of a gap in SmB_6 with decreasing temperature is associated with the Kondo effect, a many-body interaction

process between the local magnetic moments and itinerant conduction electrons [8]. At temperatures below the Kondo coherence temperature, strong hybridization of the itinerant 5d electrons and low lying local $4f$ states in SmB_6 give rise to a narrow hybridization gap of the order of 10-20 meV [9, 10]. With the chemical potential lying within this hybridization gap, the material is effectively in an insulating (semiconducting) phase [5]. At temperatures below 40 K, an in-gap resonance state emerges due to collective excitations of magnetic origin with the presence of spin-orbit coupling and valence fluctuations [11, 12]. The ground state of SmB_6 changes drastically under high pressure, the insulating gap closes around $P_c \approx 4{\text -}10$ GPa showing also a simultaneous magnetic ordering below 12 K [13, 14, 15].

Any change in the $4f$ -5d hybridization modifies the occupancy of the 4f shell, and leads to changes in the ratio of fluctuating $4f^6$ (Sm²⁺, J = 0) and $4f^5$ (Sm³⁺, $J = 5/2$) configurations. Accurate measurements of the Sm valence (a measure of the degree of localization and the total angular momentum) under different thermodynamic conditions are therefore crucial for the understanding of the various novel phases and transitions occurring in SmB_6 . Indeed, the average valence of Sm (v_{Sm}) in SmB_6 has been determined by several studies based on core level x-ray spectroscopy techniques such as x-ray photoelectron

Email addresses: emin.mijit.17@gmail.com (Emin Mijit), fabienne.duc@lncmi.cnrs.fr (Fabienne Duc), cornelius.strohm@desy.de (Cornelius Strohm)

spectroscopy (XPS) [16, 17, 18] and x-ray absorption spectroscopy (XAS) [19, 20, 21, 22, 23], reporting ambient pressure values within the range $v_{Sm} = 2.59 - 2.7$ [16, 17, 21] at room temperature and $v_{Sm} = 2.48 - 2.55$ at low temperatures (4-10 K) [17, 18, 21, 22]. In addition to the differences in the absolute values, the reported temperature dependencies of v_{Sm} appear to follow different trends [17, 19, 21, 22], even if the same spectroscopy technique was used [19, 21, 22].

In this work, we studied the pressure effects on the temperature dependence of v_{Sm} to investigate the possible correlation between Kondo insulating behavior and critical valence fluctuations (associated with a CEP) in $SmB₆$. We focused our attention on the low-pressure range of the phase diagram where the temperature induced valence changes are significant. The temperature dependence of v_{Sm} at ambient pressure has been revisited, and compared to the behaviour at higher pressure (new measurements at 1.0 and 2.0 GPa). The average valence at various temperature and pressure points has been estimated by careful analysis of the Sm L_3 –edge XAS spectra. Differences in the temperature dependence of v_{Sm} at different pressures are discussed. In order to understand the evolution of v_{Sm} towards the onset of gap-closure and magnetic ordering, we also measured its pressure dependence along an isotherm at 20 K. Additionally, we investigated the local structure of $SmB₆$ at ambient conditions using x-ray absorption fine structure (EXAFS) technique.

2. II. Experiments

High purity SmB_6 was initially synthesized in powder form by routine boron-thermal reduction of samarium oxide (Sm_2O_3) in vacuum at 1650 °C. The purity of Sm_2O_3 was 99.998 $\%$, and that for boron enriched with the ^{11}B isotope was more than 99.99 %. The obtained powder was pressed in the form of a rod, which was sintered at 1750 $\rm{^{\circ}C}$ in a vacuum and used for further growth of the $\rm{SmB_6}$ single crystal by the method of crucibleless induction zone melting under high purity argon pressure. The crystal was remelted three times before obtaining the final high quality single crystal.

Pressure and temperature dependent XAS measurements were performed at the BM23 beamline of the European Synchrotron Radiation Facility (ESRF) [24]. A double crystal monochromator equipped with two Si(111) crystals in fixed exit geometry was employed to monochromatize the incoming beam and scan the energy. The x-ray beam was focused down to $3 \times 3 \mu m^2$ using two Platinum coated mirrors in Kirkpatrick-Baez (KB) geometry. Higher order harmonics were rejected by setting these mirrors to an incidence angle of 7.0 mrad. XAS spectra were measured in transmission mode (in axial geometry through the diamond anvils) scanning across the Sm L_3 -edge. High pressures up to 8 GPa and low temperatures down to 10 K were achieved by a diamond anvil cell which was mounted inside a helium flow cryostat. In order to avoid glitches on the XAS spectra (singe crystal diamond anvils introduce glitches on the XAS spectra at x-ray energies where a Bragg condition is satisfied, because the diffracted intensity does not reach the detector and the normalization fails), the diamond anvil cell was equipped with nanopolycrystalline diamond (NPD) anvils [25, 26] of 600 μ m culet size. One of the anvils was partially perforated to reduce its absorption (total thickness of two diamonds was 1.75 mm). For the preparation of the diamond anvil cell, a 150 μ m thick stainless steel gasket was pre-indented to a final thickness of 70 μ m and laser drilled to obtain a sample chamber of about 300 μ m diameter. A rectangular piece of uniformly polished $SmB₆$ single crystal with $20 \ \mu m$ thickness was loaded into the sample chamber, together with a tiny ruby sphere for pressure determination. The rest of the sample chamber was filled with silicon oil which served as pressure transmitting medium (PTM). Use of gas PTMs was avoided to prevent the failure of the cell with perforated NPD anvil, because PTMs like He can easily penetrate into the micro-structures of NPD diamonds (it can happen also with neon depending on the quality of such diamonds). The pressure was determined from the pressure and temperature dependent shift of the ruby fluorescence spectra [27]. Sample pressure was monitored frequently (at each temperature) during the isobaric cooling runs, and kept constant at nominal values by regulating the membrane pressure. No sign of non-hydrostatisity was observed from the ruby fluorescence spectra during these cooling runs. In fact, non-hydrostatic effects of silicon was reported to be negligible even at low temperature (77 K) for $P \le 2.0$ GPa [28].

3. III. Results and discussion

3.1. A. EXAFS analysis at ambient conditions

Previous EXAFS investigations on mixed valence compounds have explored possible evidence of distorted local structures with different nearest neighbor distances corresponding to different valence state of the rare-earth ion [29, 30, 31]. However, most of the these earlier EXAFS studies have concluded that the nearest neighbor shell surrounding the rare-earth cation adopts an average distance. We measured $Sm L₃$ -edge XAS data in a wide energy range (up to 600 eV above the edge) to verify the validity of this conclusion in SmB_6 . Thanks to the NPD anvils, Sm L_3 edge XAS data could be measured without strong spurious glitches, especially in the x-ray absorption near edge structure (XANES) range where the peak fitting procedures is performed for quantitative valence analysis. However, the presence of some distortions in the higher energy postedge range could not be avoided due to the single crystalline nature of the sample itself (see Fig. S1 in the SI file). Exploitable EXAFS could only be obtained for a few data sets. Here, we provide an example EXAFS refinement for the data measured at ambient conditions. As shown in Fig.1, experimental Sm L_3 -edge EXAFS signal of

Figure 1: A typical EXAFS refinement performed for Sm L_3 -edge EXAFS data measured under ambient conditions (1bar, 300 K). The original XAS spectra from which we extracted this EXAFS signal is given in Fig. S1 (SI file). Best-fit theoretical signal includes two twobody correlations from first $(\gamma_1^{(2)})$ and second $(\gamma_2^{(2)})$ coordination shells.

SmB₆ measured at ambient conditions was refined including two two-body correlations from first $(\gamma_1^{(2)})$ and second $(\gamma_2^{(2)})$ coordination shells. The fit was performed using the GNXAS program [32, 33], by varying the atomic distances and disorder parameters concerning the first shell Sm-B and second shell Sm-Sm distributions. The coordination numbers (CN) associated with individual two-body correlations were fixed to the known values of $CN_1 = 24$ and $CN_2 = 6$ (fitting these well known numbers is not justified, considering also the short k range of the data). The agreement between the fit and the experimental data is shown in Fig. 1. From the EXAFS refinement, best-fit structural parameters such as the first shell Sm-B atomic distance $R_1 = 3.046(5)$ Å, the second shell Sm-Sm distance $R_2 = 4.12$ (1) Å, and the corresponding disorder parameters $\sigma_1^2 = 0.004(2)$ \AA^2 and $\sigma_2^2 = 0.036(10)$ \AA^2 have been obtained. Values of atomic distances obtained here are in agreement with the calculated values using crystallographic parameters reported from previous diffraction studies [34, 19, 35].

3.2. B. Temperature dependent XAS

X-ray absorption spectroscopy is highly sensitive to the valence state and electronic configuration of elements in materials of various composition [36, 37, 38]. It has been widely used as a standard tool for the studies of valence fluctuating compounds [19, 21, 22, 39, 40]. The XANES range of the normalized temperature dependent Sm L_3 edge XAS spectra measured along isobaric cooling runs at 0.0, 1.0 and 2.0 GPa are shown in Fig. 2 (a-c). In this figure, the white line range (6710-6730 eV) of each individual spectrum consists of two components, typical of mixed valence compounds. As indicated in Fig. 2 (a), the shoulder like peak at the lower energy side (~ 6715 eV) corresponds to the divalent Sm^{2+} component (with $4f^6 5d^0$ configuration), while the stronger peak at the high energy side (\sim 6722 eV) corresponds to the trivalent Sm³⁺ state (with $4f^55d^1$ configuration). One can see from Fig. 2 that the relative intensity of the Sm^{2+} peak increases upon cooling at the expense of Sm^{3+} component, indicating a more stabilized Sm^{2+} state at low temperatures. In order to quantitatively determine the average valence of Sm, the spectral weights of Sm^{2+} and Sm^{3+} configurations have been evaluated by a peak fitting procedure. Each spectral component was modeled by the sum of a Lorentz and arctangent functions to mimic the peak shape and corresponding edge jump, respectively. The spectral line shape is then fitted by the following model:

$$
f(E) = \sum_{i=2}^{3} \left[\frac{A_i(\gamma_i/2)}{(E - E_i)^2 + (\gamma_i/2)} + \frac{A_i \gamma_i}{A_2 \gamma_2 + A_3 \gamma_3} \left\{ \frac{1}{2} + \frac{1}{\pi} \arctan \frac{E - E_i - \delta}{\Gamma_i/2} \right\} \right]
$$

Here, suffix $i = 2$ and $i = 3$ represent the divalent and trivalent terms, E_i , A_i and γ_i are the energy position, intensity and full width at half maximum of the Lorentzian peaks, while Γ_i is the broadening term for the arctangents. The parameter δ is used to account for a possible slight energy shift of the continuum states of the two individual components. In this model, ratio of the white line intensity and edge jump is assumed to be equal for Sm^{2+} and Sm^{3+} configurations (around 10% of difference is approximated if one counts only the number of empty 5d holes in the final state). Nevertheless, such model functions are widely used to determine the rare-earth valence in 4f electron compounds [19, 20, 21, 22, 23, 41]. Using the best-fit A_i and γ_i parameters, v_{Sm} is given by the weighted area of the two components using the relation:

$$
v = 2 + \frac{A_3 \gamma_3}{A_2 \gamma_2 + A_3 \gamma_3}
$$

The initial fit was performed for the spectrum measured at ambient conditions, relaxing all parameters mentioned above. The resulting value $v_{Sm} = 2.60(1)$ from this

Figure 2: Temperature dependent Sm L_3 -edge XAS data measured along cooling runs at 0.0 GPa (a), 1.0 GPa (b) and 2.0 GPa (c).

fit is in good agreement with those obtained by most of the previous XAS measurements [19, 21, 22]. In order to perform a more consistent analysis of all data sets, spectra at other temperature and pressure points were fitted by relaxing A_2 and A_3 as fitting parameters, and fixing the rest of the parameters at their value at ambient conditions. Peak positions $(E_2 \text{ and } E_3)$ were relaxed (within a narrow range) at high pressures, to account the slight energy shift of spectral features induced by reduced interatomic distances.

A typical fit performed on a spectrum measured at $P = 2.0$ GPa and $T = 20$ K is shown in Fig. 3. Fig. 4 shows the temperature dependence of the average Sm valence at 0 GPa, 1.0 GPa, and 2.0 GPa obtained by fitting the data sets (in Fig. 2) with the procedures described above. At ambient pressure, the average valence and its temperature dependence are in agreement with those reported by Mizumaki et al. and Chen et al. for $T > 120$ K [21, 22], while our values deviate at lower temperatures (see the comparison from Fig. S2 in the supplementary file). On the other hand, the values for the valence obtained in this work for $T < 50$ K are close to those reported by Utsumi et al [17]. Discrepancies of the values from different studies can possibly be attributed to systematic differences in the experimental techniques (e.g. x-ray photoemission in ref. [17], dispersive XAS in ref. [22], and

standard XAS in this work and ref.[21]), fitting procedures and differences in the sample (quality and form, see supplementary information). Nevertheless, the trend of temperature dependent changes in v_{Sm} at ambient pressure is in qualitative agreement with earlier work reported by Mizumaki et al. [21], showing change of slopes at two characteristic temperatures around $T_1 \approx 120$ K and $T_2 \approx 50$ K (indicated by dashed vertical lines in Fig. 4). Characteristic temperatures T_1 and T_2 here are defined according to the maximum and minimum peaks in the second derivative of v_{Sm} vs. T curves, as shown in the inset of Fig. 4 and Fig. S3 (supplementary file).

At ambient pressure, v_{Sm} decreases slowly upon cooling until $T_1 \approx 120$ K. Below T_1 , v_{Sm} decreases more rapidly upon further cooling down to $T_2 \approx 50$ K, reflecting a more quick hybridization process between localized 4f and conducting $5d$ states (favoring the $4f^6$ -like configuration). Below $T_2 \approx 50$ K, the average valence is nearly temperature independent, stabilizing around a value of about $v_{Sm} = 2.55(1)$, until 10 K (the lowest temperature reached in this work). The temperature onset of the rapid valence change $(T_1 \approx 120 \text{ K})$ is consistent with the known Kondo coherence temperature, and the temperature onset of the semiconducting phase [9, 10, 42, 43], demonstrating the intimate correlation between the changes in the Sm valence (hybridization of $4f$ and conduction states) and the

Figure 3: A typical fit (red line) performed on a normalized $Sm L_3$ edge XAS spectrum (green circles) measured at $P = 2.0$ GPa and $T = 20$ K. Fitted spectral energy range is indicated by two vertical dashed lines.

Figure 4: Average Sm valence derived from the T dependent XAS data shown in Fig. 2. Solid line curves are guide for the eyes, obtained by fitting the data points using a arctangent function. The inset shows second derivatives of valence vs. temperature curves (solid lines) of the main figure.

formation of the Kondo gap at the Fermi level [10, 42]. While, the other characteristic temperature $T_2 \approx 50$ K, below which the valence remains stable, coincides with the temperature onset (\sim 40 K) of the in-gap state observed by Raman scattering and scanning tunneling spectroscopy measurements [11, 12]. Nearly constant non-integer values of v_{Sm} (≈ 2.55) below $T_2 \approx 50$ K indicate that SmB_6 is within valence fluctuating regime also at low temperatures well below the gap formation and in-gap state.

At higher pressures of 1.0 and 2.0 GPa, v_{Sm} also decreases upon cooling, but starting from higher room temperature values of $v_{Sm} = 2.63$ and $v_{Sm} = 2.65$, respectively. However, change of slopes (around T_1 and T_2) seem to be suppressed with the increase of pressure, changing to an almost monotonic decreasing trend at 2.0 GPa. The metal-insulator transition (MIT) in SmB_6 is known to occur within 4-10 GPa range depending on the experimental conditions [13, 14, 15]. Under quasi-hydrostatic conditions (e.g, when a solid PTM like NaCl is used), MIT occurs at lower pressures (as low as 4.0 GPa) [15]. The onset pressure of the MIT is pushed up to 10 GPa in case of hydrostatic experiments [14]. The liquid PTM (silicon oil) that we used in this study was reported to be hydrostatic below 2.0 GPa at 77 K [28]. Thus development of considerable deviatoric stress is not expected from our cooling runs at constant pressures. Therefore, less pronounced slope changes (between 50-120 K) in the valence vs. T curves that we observed here is not related with the MIT or with pressure in-homogeneity. Instead, this behavior is reminiscent of what happens in the typical Ce, Yb and Eu valence transition systems (e.g. elemental Ce metal, $YbInCu₄$ and $EuRh₂Si₂$) which show sharp valence transitions at lower pressures but move to a gradual valence crossover regime under physical or chemical pressure [44, 45, 46, 47, 48, 49]. For example, in the case of Ce metal, the valence change and thus the decrease of the volume become more continuous upon cooling at pressures higher than 2.0 GPa, after escaping from the pressure-temperature ranges of the $\gamma - \alpha$ transition line and its CEP (at about 600 K and 2.0) GPa) [44, 45]. Similar behavior also occurs in compounds like YbInCu₄ and EuRh₂Si₂, where the temperature dependent valence change becomes more continuous under physical or chemical pressure, after exceeding the domain of the existing CEP [46, 47, 48, 49]. The existence and location of such a CEP plays a decisive role for the emergence of various exotic phases in valence fluctuating and heavy fermion compounds (such as unconventional superconductivity) [1, 2, 3]. We therefore can speculate that the gap formation and Kondo insulator behaviour in $SmB₆$ is also associated with an underlying first order valence transition. If this is the case, the underlying CEP would be expected to be located at negative pressures due to the fact that the observed anomalies in the temperature dependent valence change at ambient pressure are still not very sharp. In addition, no drastic volume change (characteristic of first order valence transitions) was observed in $SmB₆$ at ambient pressure. In fact, the possible existence

of such an underlying first order phase transition and CEP was also discussed and proposed by a recent theoretical work [50].

Figure 5: Pressure dependence of Sm L3-edge XAS spectra measured along the isotherm at 20 K.

3.3. C. Pressure dependent XAS

Several pressure dependent Sm L_3 -edge XANES spectra measured along the 20 K isotherm are shown in Fig. 5. The application of pressure stabilizes the Sm^{3+} state as indicated by the increased weight of the Sm^{3+} at the expense of Sm^{2+} peak. The pressure dependence of v_{Sm} was evaluated using the peak fitting procedure described above. For this set of high pressure data, E_2 and E_3 were relaxed with minor freedom in addition to the fitting parameters A_2 and A_3 . This was necessary to account for the pressure induced shift of the resonance peaks introduced by the decrease of atomic distances (energy position of the XAS resonance peaks is inversely proportional to the square of atomic distances, according to Natoli's rule: $(E_{peak} - E_{edge}) \cdot R^2 = constant$ [51]).

In Fig. 6, the average Sm valence v_{Sm} is plotted as a function of pressure. As we can see, the pressure dependence of v_{Sm} and its absolute values obtained in this work are in agreement with those obtained by Chen at al. at 8 K [22]. The trend of v_{Sm} upon compression is similar to the behavior observed at room temperature [52], but very different from the result of another room temperature measurement (in which v_{Sm} increase rapidly above 4.0 GPa and approaches to 3.0 around 8-10 GPa) [15]. Possibly, such disagreement originated from the employment of different pressure mediums (NaCl vs. silicon oil) and fitting procedures (one arctangent function instead of two) used

Figure 6: Pressure dependence of the average Sm valence (at 20 K) obtained from this work compared with the pressure dependent Sm valence (at 8 K) reported in ref. [22].

in ref. $[15]$. From our data, v_{Sm} increases upon compression without noticeable anomaly, and reaches a value of $v_{Sm} \approx 2.670(5)$ at 8.0 GPa. The increase of valence, and thus the Sm^{3+} configuration with angular momentum $J = 5/2$ is in line with the non-magnetic to magnetic transition accompanied by gap closure in 6-10 GPa pressure range [13, 14]. However, the $v_{Sm} \approx 2.70(1)$ at a pressure near the magnetic transition pressure remains far below the integer value $(3+)$. This is markedly different from the typical valence fluctuating compounds which favour a 4f electron configuration with near integer valence in the high pressure magnetic phase [53, 54, 55, 56, 57]. These results are in agreement with findings reported in previous high-pressure experiments on $SmB₆$. [23, 52].

4. IV. Conclusion

In summary, we have investigated the pressure and temperature induced valence changes in the Kondo insulator SmB_6 along several isobaric cooling runs and an isothermal compression using XAS. The average valence of Sm at various pressure and temperature conditions have been extracted from high quality XAS data by peak fitting procedures. The changes of slope in the temperature dependence of v_{Sm} were discussed in relation with the formation of the hybridization gap and in-gap states. Differences in the v_{Sm} versus temperature curves at different pressures were discussed in relation to an underlying first order valence transition. We suggest that the critical end point of this first order valence transition would be located at negative pressures. The pressure dependence of the Sm valence along the isotherm at 20K has shown that v_{Sm} is far below the expected value of $+3$ near the pressure onset of the long range magnetic ordering. The local structure of $SmB₆$ at ambient conditions was studied using EXAFS signals. We extracted values for radial distribution of the first and second coordination shells. These values (especially atomic distances) are in agreement with the results of previous diffraction experiments. A more profound temperature and pressure dependent EXAFS study (using powder samples) would be desirable in order to better quantify the local structural changes associated with the gap formation and valence fluctuations in $SmB₆$.

Acknowledgments

We acknowledge European Synchrotron Radiation Facility (ESRF) for the provision of beam-times (in-house) at the BM23 beamline. We thank Andrea Di Cicco (University of Camerino, Italy) and Fabio Iesari (University of Toyama, Japan) for their advices during the data analysis. The authors also acknowledge the support from ISABEL project, funded by the European Union's Horizon 2020 research and innovation programme (Grant Agreement No. 871106).

References

- [1] G. W. Scheerer, Z. Ren, S. Watanabe, G. Lapertot, D. Aoki, D. Jaccard, K. Miyake, The dominant role of critical valence fluctuations on high tc superconductivity in heavy fermions, npj Quantum Materials 3 (41) (2018) 41.
- [2] S. Watanabe, K. Miyake, [Quantum valence criticality as an ori](https://link.aps.org/doi/10.1103/PhysRevLett.105.186403)[gin of unconventional critical phenomena,](https://link.aps.org/doi/10.1103/PhysRevLett.105.186403) Phys. Rev. Lett. 105 (2010) 186403. [doi:10.1103/PhysRevLett.105.186403](https://doi.org/10.1103/PhysRevLett.105.186403). URL [https://link.aps.org/doi/10.1103/PhysRevLett.105.](https://link.aps.org/doi/10.1103/PhysRevLett.105.186403) [186403](https://link.aps.org/doi/10.1103/PhysRevLett.105.186403)
- [3] S. Watanabe, K. Miyake, Roles of critical valence fluctuations in ce-and yb-based heavy fermion metals, Journal of Physics: Condensed Matter 23 (9) (2011) 094217.
- [4] A. Menth, E. Buehler, T. H. Geballe, [Magnetic and semi](https://link.aps.org/doi/10.1103/PhysRevLett.22.295)conducting properties of smb_6 , Phys. Rev. Lett. 22 (1969) 295–297. [doi:10.1103/PhysRevLett.22.295](https://doi.org/10.1103/PhysRevLett.22.295). URL [https://link.aps.org/doi/10.1103/PhysRevLett.22.](https://link.aps.org/doi/10.1103/PhysRevLett.22.295) [295](https://link.aps.org/doi/10.1103/PhysRevLett.22.295)
- [5] P. S. Riseborough, Heavy fermion semiconductors, Advances in Physics 49 (3) (2000) 257–320.
- [6] M. Dzero, K. Sun, V. Galitski, P. Coleman, [Topological kondo](https://link.aps.org/doi/10.1103/PhysRevLett.104.106408) [insulators,](https://link.aps.org/doi/10.1103/PhysRevLett.104.106408) Phys. Rev. Lett. 104 (2010) 106408. [doi:10.1103/](https://doi.org/10.1103/PhysRevLett.104.106408) [PhysRevLett.104.106408](https://doi.org/10.1103/PhysRevLett.104.106408). URL [https://link.aps.org/doi/10.1103/PhysRevLett.104.](https://link.aps.org/doi/10.1103/PhysRevLett.104.106408) [106408](https://link.aps.org/doi/10.1103/PhysRevLett.104.106408)
- [7] S. Wolgast, i. m. c. b. u. i. e. i. f. Kurdak, K. Sun, J. W. Allen, D.-J. Kim, Z. Fisk, [Low-temperature surface conduction](https://link.aps.org/doi/10.1103/PhysRevB.88.180405) in the kondo insulator smb_6 , Phys. Rev. B 88 (2013) 180405. [doi:10.1103/PhysRevB.88.180405](https://doi.org/10.1103/PhysRevB.88.180405).
URL https://link.aps.org/ [https://link.aps.org/doi/10.1103/PhysRevB.88.](https://link.aps.org/doi/10.1103/PhysRevB.88.180405) [180405](https://link.aps.org/doi/10.1103/PhysRevB.88.180405)
- [8] L. Kouwenhoven, L. Glazman, Revival of the kondo effect, Physics world 14 (1) (2001) 33.
- [9] T. Kasuya, K. Takegahara, T. Fujita, T. Tanaka, E. Bannai, Valence fluctuating state in smb6, Le Journal de Physique Colloques 40 (C5) (1979) C5–308.
- [10] S. Nozawa, T. Tsukamoto, K. Kanai, T. Haruna, S. Shin, S. Kunii, Ultrahigh-resolution and angle-resolved photoemission study of smb6, Journal of Physics and Chemistry of Solids 63 (6- 8) (2002) 1223–1226.
- [11] P. Nyhus, S. L. Cooper, Z. Fisk, J. Sarrao, [Low-energy excita](https://link.aps.org/doi/10.1103/PhysRevB.55.12488)[tions of the correlation-gap insulator](https://link.aps.org/doi/10.1103/PhysRevB.55.12488) $smb₆$:ffa light-scattering [study,](https://link.aps.org/doi/10.1103/PhysRevB.55.12488) Phys. Rev. B 55 (1997) 12488–12496. [doi:10.1103/](https://doi.org/10.1103/PhysRevB.55.12488)

[PhysRevB.55.12488](https://doi.org/10.1103/PhysRevB.55.12488).

URL <https://link.aps.org/doi/10.1103/PhysRevB.55.12488>

[12] W. Ruan, C. Ye, M. Guo, F. Chen, X. Chen, G.-M. Zhang, Y. Wang, [Emergence of a coherent in-gap state in the](https://link.aps.org/doi/10.1103/PhysRevLett.112.136401) $smb₆$ [kondo insulator revealed by scanning tunneling spectroscopy,](https://link.aps.org/doi/10.1103/PhysRevLett.112.136401) Phys. Rev. Lett. 112 (2014) 136401. [doi:10.1103/PhysRevLett.](https://doi.org/10.1103/PhysRevLett.112.136401) [112.136401](https://doi.org/10.1103/PhysRevLett.112.136401). URL [https://link.aps.org/doi/10.1103/PhysRevLett.112.](https://link.aps.org/doi/10.1103/PhysRevLett.112.136401)

[136401](https://link.aps.org/doi/10.1103/PhysRevLett.112.136401)

- [13] A. Barla, J. Derr, J. P. Sanchez, B. Salce, G. Lapertot, B. P. Doyle, R. Rüffer, R. Lengsdorf, M. M. Abd-Elmeguid, J. Flouquet, [High-pressure ground state of](https://link.aps.org/doi/10.1103/PhysRevLett.94.166401) smb_6 : Electronic [conduction and long range magnetic order,](https://link.aps.org/doi/10.1103/PhysRevLett.94.166401) Phys. Rev. Lett. 94 (2005) 166401. [doi:10.1103/PhysRevLett.94.166401](https://doi.org/10.1103/PhysRevLett.94.166401). URL [https://link.aps.org/doi/10.1103/PhysRevLett.94.](https://link.aps.org/doi/10.1103/PhysRevLett.94.166401) [166401](https://link.aps.org/doi/10.1103/PhysRevLett.94.166401)
- [14] J. Derr, G. Knebel, D. Braithwaite, B. Salce, J. Flouquet, K. Flachbart, S. Gabáni, N. Shitsevalova, [From unconventional](https://link.aps.org/doi/10.1103/PhysRevB.77.193107) [insulating behavior towards conventional magnetism in the](https://link.aps.org/doi/10.1103/PhysRevB.77.193107) intermediate-valence compound smb_6 , Phys. Rev. B 77 (2008) 193107. [doi:10.1103/PhysRevB.77.193107](https://doi.org/10.1103/PhysRevB.77.193107). URL [https://link.aps.org/doi/10.1103/PhysRevB.77.](https://link.aps.org/doi/10.1103/PhysRevB.77.193107) [193107](https://link.aps.org/doi/10.1103/PhysRevB.77.193107)
- [15] Y. Zhou, Q. Wu, P. F. Rosa, R. Yu, J. Guo, W. Yi, S. Zhang, Z. Wang, H. Wang, S. Cai, K. Yang, A. Li, Z. Jiang, S. Zhang, X. Wei, Y. Huang, P. Sun, Y. feng Yang, Z. Fisk, Q. Si, Z. Zhao, L. Sun, [Quantum phase transition and destruction of kondo](https://www.sciencedirect.com/science/article/pii/S2095927317305248) [effect in pressurized smb6,](https://www.sciencedirect.com/science/article/pii/S2095927317305248) Science Bulletin 62 (21) (2017) 1439– 1444. [doi:https://doi.org/10.1016/j.scib.2017.10.008](https://doi.org/https://doi.org/10.1016/j.scib.2017.10.008). URL [https://www.sciencedirect.com/science/article/pii/](https://www.sciencedirect.com/science/article/pii/S2095927317305248) [S2095927317305248](https://www.sciencedirect.com/science/article/pii/S2095927317305248)
- [16] J. W. Allen, L. I. Johansson, I. Lindau, S. B. Hagstrom, [Surface](https://link.aps.org/doi/10.1103/PhysRevB.21.1335) mixed valence in sm and smb_6 , Phys. Rev. B 21 (1980) 1335– 1343. [doi:10.1103/PhysRevB.21.1335](https://doi.org/10.1103/PhysRevB.21.1335). URL <https://link.aps.org/doi/10.1103/PhysRevB.21.1335>
- [17] Y. Utsumi, D. Kasinathan, K.-T. Ko, S. Agrestini, M. Haverkort, S. Wirth, Y. Wu, K. Tsuei, D. Kim, Z. Fisk, et al., Bulk and surface electronic properties of smb 6: A hard x-ray photoelectron spectroscopy study, Physical Review B 96 (15) (2017) 155130.
- [18] P. Lutz, M. Thees, T. Peixoto, B. Kang, B. Cho, C. H. Min, F. Reinert, Valence characterisation of the subsurface region in, Philosophical Magazine 96 (31) (2016) 3307–3321.
- [19] J.-m. Tarascon, Y. Isikawa, B. Chevalier, J. Etourneau, P. Hagenmuller, M. Kasaya, Temperature dependence of the samarium oxidation state in smb6 and sm1-xlaxb6, Journal de Physique 41 (10) (1980) 1141–1145.
- [20] E. Beaurepaire, J. Kappler, G. Krill, X-ray-absorption nearedge structure study in mixed-valent samarium systems, Physical Review B 41 (10) (1990) 6768.
- [21] M. Mizumaki, S. Tsutsui, F. Iga, Temperature dependence of sm valence in smb6 studied by x-ray absorption spectroscopy, in: Journal of Physics: Conference Series, Vol. 176, IOP Publishing, 2009, p. 012034.
- [22] K. Chen, T. Weng, G. Schmerber, V. Gurin, J.-P. Kappler, Q. Kong, F. Baudelet, A. Polian, L. Nataf, Surface-and pressure-induced bulk kondo breakdown in smb 6, Physical Review B 97 (23) (2018) 235153.
- [23] N. Emi, N. Kawamura, M. Mizumaki, T. Koyama, N. Ishimatsu, G. Pristáš, T. Kagayama, K. Shimizu, Y. Osanai, F. Iga, et al., Kondo-like behavior near the magnetic instability in smb 6: Temperature and pressure dependences of the sm valence, Physical Review B 97 (16) (2018) 161116.
- [24] O. Mathon, A. Beteva, J. Borrel, D. Bugnazet, S. Gatla, R. Hino, I. Kantor, T. Mairs, M. Munoz, S. Pasternak, et al., The time-resolved and extreme conditions xas (texas) facility at the european synchrotron radiation facility: the general-purpose exafs bending-magnet beamline bm23, Journal of synchrotron radiation 22 (6) (2015) 1548–1554.
- [25] T. Irifune, A. Kurio, S. Sakamoto, T. Inoue, H. Sumiya, Materials: Ultrahard polycrystalline diamond from graphite, Nature

421 (6923) (2003) 599.

- [26] N. Ishimatsu, K. Matsumoto, H. Maruyama, N. Kawamura, M. Mizumaki, H. Sumiya, T. Irifune, Glitch-free x-ray absorption spectrum under high pressure obtained using nanopolycrystalline diamond anvils, Journal of synchrotron radiation 19 (5) (2012) 768–772.
- [27] F. Datchi, A. Dewaele, P. Loubeyre, R. Letoullec, Y. Le Godec, B. Canny, Optical pressure sensors for high-pressure–hightemperature studies in a diamond anvil cell, High Pressure Research 27 (4) (2007) 447–463.
- [28] N. Tateiwa, Y. Haga, Evaluations of pressure-transmitting media for cryogenic experiments with diamond anvil cell, Review of Scientific Instruments 80 (12) (2009).
- [29] R. M. Martin, J. B. Boyce, J. W. Allen, F. Holtzberg, [Extended](https://link.aps.org/doi/10.1103/PhysRevLett.44.1275) [x-ray-absorption fine-structure studies of electron-lattice cor](https://link.aps.org/doi/10.1103/PhysRevLett.44.1275)[relations in mixed-valence](https://link.aps.org/doi/10.1103/PhysRevLett.44.1275) $sm_{0.75}y_{0.25}s$, Phys. Rev. Lett. 44 (1980) 1275–1278. [doi:10.1103/PhysRevLett.44.1275](https://doi.org/10.1103/PhysRevLett.44.1275). URL [https://link.aps.org/doi/10.1103/PhysRevLett.44.](https://link.aps.org/doi/10.1103/PhysRevLett.44.1275) [1275](https://link.aps.org/doi/10.1103/PhysRevLett.44.1275)
- [30] B. Lengeler, G. Materlik, J. E. Müller, l[-edge x-ray absorption](https://link.aps.org/doi/10.1103/PhysRevB.28.2276) [spectra of](https://link.aps.org/doi/10.1103/PhysRevB.28.2276) γ −and α −cerium, Phys. Rev. B 28 (1983) 2276–2278. [doi:10.1103/PhysRevB.28.2276](https://doi.org/10.1103/PhysRevB.28.2276). URL <https://link.aps.org/doi/10.1103/PhysRevB.28.2276>
- [31] G. Krill, J. Kappler, M. Ravet, C. Godart, J. Senateur, Local environment effects in mixed valent rare-earth systems studied by exafs, Journal of magnetism and magnetic materials 47 (1985) 190–196.
- [32] A. Filipponi, A. Di Cicco, C. R. Natoli, X-ray absorption spectroscopy and n-body distribution functions in condensed matter (I): theory., Phys. Rev. B 52 (1995) 15122–15134.
- [33] A. Filipponi, A. Di Cicco, X-ray absorption spectroscopy and n-body distribution functions in condensed matter (II): dataanalysis and applications, Phys. Rev. B 52 (1995) 15135.
- [34] N. Brandt, V. Moshchalkov, S. Pashkevich, M. Vybornov, M. Semenov, T. Kolobyanina, E. Konovalova, Y. B. Paderno, High pressure studies of cerium hexaboride, Solid state communications 56 (11) (1985) 937–941.
- [35] V. Trounov, A. Malyshev, D. Y. Chernyshov, M. Korsukova, V. Gurin, L. Aslanov, V. Chernyshev, Temperature dependences of the parameters of atoms in the crystal structure of the intermediate-valence semiconductor smb6: investigation by high-resolution powder neutron diffraction, Journal of Physics: Condensed Matter 5 (16) (1993) 2479.
- [36] K. Chen, Y. Mijiti, S. Agrestini, S.-C. Liao, X. Li, J. Zhou, A. Di Cicco, F. Baudelet, L. H. Tjeng, Z. Hu, Valence state of pb in transition metal perovskites pbtmo3 (tm= ti, ni) determined from x-ray absorption near-edge spectroscopy, physica status solidi (b) 255 (6) (2018) 1800014.
- [37] J. García, G. Subías, J. Blasco, Xas studies on mixed valence oxides, X-Ray Absorption and X-Ray Emission Spectroscopy: Theory and Applications (2016) 459–484.
- [38] E. Mijit, K. Chen, J. a. E. F. S. Rodrigues, Z. Hu, L. Nataf, A. Trapananti, A. Di Cicco, F. Baudelet, [Crystal and electronic](https://link.aps.org/doi/10.1103/PhysRevB.103.024105) structure of co3o⁴ [spinel under pressure probed by xanes](https://link.aps.org/doi/10.1103/PhysRevB.103.024105) [and raman spectroscopy,](https://link.aps.org/doi/10.1103/PhysRevB.103.024105) Phys. Rev. B 103 (2021) 024105. [doi:10.1103/PhysRevB.103.024105](https://doi.org/10.1103/PhysRevB.103.024105). URL [https://link.aps.org/doi/10.1103/PhysRevB.103.](https://link.aps.org/doi/10.1103/PhysRevB.103.024105) [024105](https://link.aps.org/doi/10.1103/PhysRevB.103.024105)
- [39] C. Rao, D. Sarma, P. Sarode, E. Sampathkumaran, L. Gupta, R. Vijayaraghavan, Valence fluctuation in some yb intermetallics by x-ray photoemission and x-ray absorption, Chemical Physics Letters 76 (3) (1980) 413–415.
- [40] H. Launois, M. Rawiso, E. Holland-Moritz, R. Pott, D. Wohlleben, [X-ray absorption study of mixed](https://link.aps.org/doi/10.1103/PhysRevLett.44.1271)[valence tmse,](https://link.aps.org/doi/10.1103/PhysRevLett.44.1271) Phys. Rev. Lett. 44 (1980) 1271–1275. [doi:10.1103/PhysRevLett.44.1271](https://doi.org/10.1103/PhysRevLett.44.1271).
URL https://link.aps.org/doi/ [https://link.aps.org/doi/10.1103/PhysRevLett.44.](https://link.aps.org/doi/10.1103/PhysRevLett.44.1271) [1271](https://link.aps.org/doi/10.1103/PhysRevLett.44.1271)
- [41] K. Matsubayashi, T. Hirayama, T. Yamashita, S. Ohara, N. Kawamura, M. Mizumaki, N. Ishimatsu, S. Watanabe, K. Kitagawa, Y. Uwatoko, [Pressure-induced valence crossover](https://link.aps.org/doi/10.1103/PhysRevLett.114.086401)

[and novel metamagnetic behavior near the antiferromagnetic](https://link.aps.org/doi/10.1103/PhysRevLett.114.086401) [quantum phase transition of](https://link.aps.org/doi/10.1103/PhysRevLett.114.086401) ybni₃ga₉, Phys. Rev. Lett. 114 (2015) 086401. [doi:10.1103/PhysRevLett.114.086401](https://doi.org/10.1103/PhysRevLett.114.086401). URL [https://link.aps.org/doi/10.1103/PhysRevLett.114.](https://link.aps.org/doi/10.1103/PhysRevLett.114.086401) [086401](https://link.aps.org/doi/10.1103/PhysRevLett.114.086401)

- [42] J. Yamaguchi, A. Sekiyama, M. Kimura, H. Sugiyama, Y. Tomida, G. Funabashi, S. Komori, T. Balashov, W. Wulfhekel, T. Ito, et al., Different evolution of the intrinsic gap in strongly correlated smb6 in contrast to ybb12, New Journal of Physics 15 (4) (2013) 043042.
- [43] J. Jiang, S. Li, T. Zhang, Z. Sun, F. Chen, Z. Ye, M. Xu, Q. Ge, S. Tan, X. Niu, et al., Observation of possible topological in-gap surface states in the kondo insulator smb6 by photoemission, Nature communications 4 (1) (2013) 1–8.
- [44] K. A. Gschneidner, J.-C. G. Bunzli, V. K. Pecharsky, Handbook on the physics and chemistry of rare earths, Vol. 34, Elsevier, 2005.
- [45] B. L. Davis, L. H. Adams, X-ray diffraction evidence for a critical end point for cerium i and cerium ii, Journal of Physics and Chemistry of Solids 25 (4) (1964) 379–388.
- [46] J. L. Sarrao, C. D. Immer, C. L. Benton, Z. Fisk, J. M. Lawrence, D. Mandrus, J. D. Thompson, [Evolution from](https://link.aps.org/doi/10.1103/PhysRevB.54.12207) [first-order valence transition to heavy-fermion behavior in](https://link.aps.org/doi/10.1103/PhysRevB.54.12207) $y \text{bin}_{1-x}$ ag_xcu₄, Phys. Rev. B 54 (1996) 12207–12211. [doi:](https://doi.org/10.1103/PhysRevB.54.12207) [10.1103/PhysRevB.54.12207](https://doi.org/10.1103/PhysRevB.54.12207). URL <https://link.aps.org/doi/10.1103/PhysRevB.54.12207>

[47] S. Watanabe, A. Tsuruta, K. Miyake, J. Flouquet, Valence fluc-

- tuations revealed by magnetic field and pressure scans: Comparison with experiments in ybxcu4 ($x=$ in, ag, cd) and ceyin5 $(y=$ ir, rh), Journal of the Physical Society of Japan 78 (10) (2009) 104706.
- [48] S. Seiro, C. Geibel, From stable divalent to valence-fluctuating behaviour in eu (rh1- xirx) 2si2 single crystals, Journal of Physics: Condensed Matter 23 (37) (2011) 375601.
- [49] F. Honda, K. Okauchi, A. Nakamura, D. Li, D. Aoki, H. Akamine, Y. Ashitomi, M. Hedo, T. Nakama, Y. Onuki, Pressure-induced valence transition and characteristic electronic states in eurh2si2, journal of the physical society of japan 85 (6) (2016) 063701.
- [50] J.-T. Zhuang, X.-J. Zheng, Z.-Y. Wang, X. Ming, H. Li, Y. Liu, H.-F. Song, Valence transition in topological kondo insulator, Journal of Physics: Condensed Matter 32 (3) (2020) 035602.
- [51] C. Natoli, Distance dependence of continuum and bound state of excitonic resonances in x-ray absorption near edge structure (xanes), in: EXAFS and near edge structure III, Springer, 1984, pp. 38–42.
- [52] N. P. Butch, J. Paglione, P. Chow, Y. Xiao, C. A. Marianetti, C. H. Booth, J. R. Jeffries, [Pressure-resistant intermediate va](https://link.aps.org/doi/10.1103/PhysRevLett.116.156401)[lence in the kondo insulator](https://link.aps.org/doi/10.1103/PhysRevLett.116.156401) smb_6 , Phys. Rev. Lett. 116 (2016) 156401. [doi:10.1103/PhysRevLett.116.156401](https://doi.org/10.1103/PhysRevLett.116.156401). URL [https://link.aps.org/doi/10.1103/PhysRevLett.116.](https://link.aps.org/doi/10.1103/PhysRevLett.116.156401) [156401](https://link.aps.org/doi/10.1103/PhysRevLett.116.156401)
- [53] A. Fernandez-Pañella, V. Balédent, D. Braithwaite, L. Paolasini, R. Verbeni, G. Lapertot, J.-P. Rueff, [Valence instability](https://link.aps.org/doi/10.1103/PhysRevB.86.125104) of ybcu2si² [through its magnetic quantum critical point,](https://link.aps.org/doi/10.1103/PhysRevB.86.125104) Phys. Rev. B 86 (2012) 125104. [doi:10.1103/PhysRevB.86.125104](https://doi.org/10.1103/PhysRevB.86.125104). URL [https://link.aps.org/doi/10.1103/PhysRevB.86.](https://link.aps.org/doi/10.1103/PhysRevB.86.125104) [125104](https://link.aps.org/doi/10.1103/PhysRevB.86.125104)
- [54] H. Yamaoka, I. Jarrige, N. Tsujii, J.-F. Lin, N. Hiraoka, H. Ishii, K.-D. Tsuei, [Temperature and pressure-induced](https://link.aps.org/doi/10.1103/PhysRevB.82.035111) valence transitions in $ybni_2ge_2$ and $ybpd_2si_2$, Phys. Rev. B 82 (2010) 035111. [doi:10.1103/PhysRevB.82.035111](https://doi.org/10.1103/PhysRevB.82.035111). URL [https://link.aps.org/doi/10.1103/PhysRevB.82.](https://link.aps.org/doi/10.1103/PhysRevB.82.035111) [035111](https://link.aps.org/doi/10.1103/PhysRevB.82.035111)
- [55] H. Yamaoka, N. Tsujii, Y. Utsumi, H. Sato, I. Jarrige, Y. Yamamoto, J.-F. Lin, N. Hiraoka, H. Ishii, K.-D. Tsuei, J. Mizuki, [Valence transitions in the heavy-fermion compound ybcual as a](https://link.aps.org/doi/10.1103/PhysRevB.87.205120) [function of temperature and pressure,](https://link.aps.org/doi/10.1103/PhysRevB.87.205120) Phys. Rev. B 87 (2013) 205120. [doi:10.1103/PhysRevB.87.205120](https://doi.org/10.1103/PhysRevB.87.205120). URL [https://link.aps.org/doi/10.1103/PhysRevB.87.](https://link.aps.org/doi/10.1103/PhysRevB.87.205120) [205120](https://link.aps.org/doi/10.1103/PhysRevB.87.205120)
- [56] H. Yamaoka, Y. Zekko, A. Kotani, I. Jarrige, N. Tsujii, J.-F. Lin, J. Mizuki, H. Abe, H. Kitazawa, N. Hiraoka, H. Ishii, K.-D. Tsuei, Electronic transitions in ${\rm cepd_2si_2}$ studied [by resonant x-ray emission spectroscopy at high pressures](https://link.aps.org/doi/10.1103/PhysRevB.86.235131) [and low temperatures,](https://link.aps.org/doi/10.1103/PhysRevB.86.235131) Phys. Rev. B 86 (2012) 235131. [doi:10.1103/PhysRevB.86.235131](https://doi.org/10.1103/PhysRevB.86.235131).
URL https://link.aps.org/ [https://link.aps.org/doi/10.1103/PhysRevB.86.](https://link.aps.org/doi/10.1103/PhysRevB.86.235131) [235131](https://link.aps.org/doi/10.1103/PhysRevB.86.235131)
- [57] H. Yamaoka, Y. Ikeda, I. Jarrige, N. Tsujii, Y. Zekko, Y. Yamamoto, J. Mizuki, J.-F. Lin, N. Hiraoka, H. Ishii, K.-D. Tsuei, T. C. Kobayashi, F. Honda, Y. Onuki, [Role of valence fluc](https://link.aps.org/doi/10.1103/PhysRevLett.113.086403)[tuations in the superconductivity of ce122 compounds,](https://link.aps.org/doi/10.1103/PhysRevLett.113.086403) Phys. Rev. Lett. 113 (2014) 086403. [doi:10.1103/PhysRevLett.113.](https://doi.org/10.1103/PhysRevLett.113.086403) [086403](https://doi.org/10.1103/PhysRevLett.113.086403).

URL [https://link.aps.org/doi/10.1103/PhysRevLett.113.](https://link.aps.org/doi/10.1103/PhysRevLett.113.086403) [086403](https://link.aps.org/doi/10.1103/PhysRevLett.113.086403)