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Electronic supplementary information (ESI) for the article entitled "Thermoelectric properties of heavy fermion CeRhIn₅ using density functional theory combined with semiclassical Boltzmann theory"

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This electronic supplementary information (ESI) is provided to support the results and discussion presented in the main paper. The calculated band structures and densities of states (DOSs) are presented using three different exchange-correlation functionals with three different degrees of localization. Then, the Kohen-Sham Hamiltonian using each of these functionals is applied to study the electronic structures of CeRhIn₅ with three different volumes. Thus, 9 band structures and 9 DOSs are shown for spin up. Similarly, 9 band structures and 9 DOSs are presented for spin down. These 36 figures are presented in this ESI to concise and make straightforward the electronic structure discussion of the main paper. Instead in the main paper, extracted quantitative values from these figures are quantitatively discussed to increase the accuracy of the discussion. In this ESI, two computer programs and a flowchart are also appended to numerically support thermoelectric values presented in the main paper. This will show how the data are extracted from the output file of BoltzTrap code and make them easily reproducible by the others. These programs are provided because in most of the regular thermoelectric studies by BoltzTrap using its default outputs, the thermoelectric properties are not presented versus temperature. However, our calculated thermoelectric properties are plotted here as functions of temperature due to the main goal of the paper which is determining the thermoelectric efficiency of the system under study.

1 Crystal structure

The chemical structure of the CeRhIn₅ compound, as shown in Fig. 1, crystallizes in P4/mmm space group number 123.¹⁻³ The experimental lattice parameters of the compound were measured to be $a = 4.656$ (Å) and $c = 7.542$ (Å).^{2,3}

2 Post processing calculations

CeRhIn₅ is a well-known heavy-fermion antiferromagnet at room temperature which crystallizes in P4/mmm space group number 123.¹⁻³ The chemical structure of this material is shown in Fig. 1.

3 Electronic structure

We have calculated the band structures using PBE-GGA, PBE-GGA+U with $U_{eff}=5.5$ eV, and hybrid B3PW91 with $\alpha=0.3$ for CeRhIn₅ compound having three different volumes. The first volume is the experimental volume at zero pressure. The second and

third volumes are 2% and 5% smaller than the first volume, respectively. The calculated band structures are presented in Figs. 2 and 3, respectively. In these figures, the E_F is set to zero. Furthermore, contributions of the 4f-Ce states are characterized by the thickness of the bands; the larger the band thickness, the higher the contribution of the 4f-Ce states to the band.

The results show that the pressure cannot considerably change the band structures of the system, as can be seen from any rows of Fig. 2 or Fig. 3. For example, if we consider the first row of Fig. 2, we clearly observe that most of the 4f-Ce states are very closely distributed around the Fermi level in Figs. 2(a11), (a12) and (a13). This can be also seen in the second and third rows of Fig. 2 or Fig. 3. This observation implies that the distribution of the 4f-Ce states is not significantly changed when we apply pressure theoretically withoth considering the changes made in the degree of localization due to our applied pressure. In contrast to the pressure, however, the degree of localization can more considerably affect the band structures, as can be seen from any columns of Fig. 2 or Fig. 3. For example, if we consider the first column of Fig. 2, we clearly observe that the distribution of the

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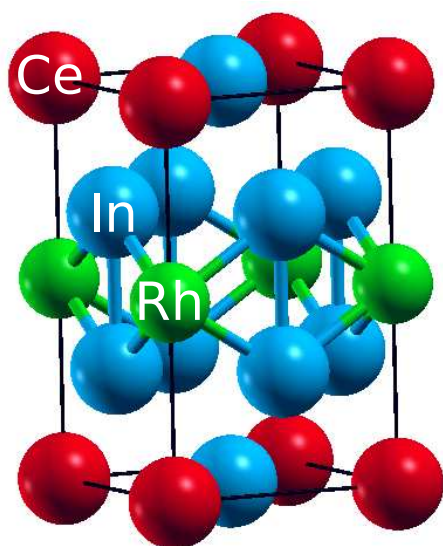


Fig. 1 Chemical structure of the CeRhIn₅ compound.

4f-Ce states is considerably affected by changing the functionals and thereby the degree of localization in Figs. 2(a11), (a21) and (a31). This can be also seen in the second and third columns of Fig. 2 or Fig. 3.

Total and 4f-Ce as well as 4d-Rh partials DOSs of CeRhIn₅ are also calculated using PBE-GGA, GGA+U with $U_{eff}=5.5$ eV, and hybrid B3PW91 with $\alpha=0.3$. The results for the three aforementioned volumes of the compound are shown in Figs. 4 and 5. The Fermi level is set to zero, as denoted by the vertical dashed line.

The results, consistent with the band structure results, implies that the total and partial DOSs of CeRhIn₅ are not drastically changed by pressure. The total and partial DOSs are very similar for the three considered volumes of the compound, as can be seen from any rows of Fig. 4 or Fig. 5.

However, the DOSs, as discussed below, show that the degree of localization more significantly affects the partial and total DOSs of CeRhIn₅ than pressure. The results show that the 4f-Ce DOSs and as a result total DOSs around E_F are splitted by GGA+U in the three considered volumes. The GGA+U functional causes the occupied (unoccupied) total and 4f-Ce DOSs to shift towards lower (higher) energies than E_F with respect to the DOSs predicted by PBE-GGA. These shifts lead to a reduction of DOSs at the Fermi level. These results are in agreement with the previous calculations for other strongly correlated cases.^{4,5} Similar to the GGA+U approach, the hybrid B3PW91 functional splits the occupied and unoccupied total and partial 4f-Ce DOSs compared to the PBE-GGA DOSs, see third and first rows of Fig. 4 or Fig. 5. However, the B3PW91 splitting is less than the GGA+U splitting. Thus, occupied and unoccupied states remain closer to the Fermi level after applying B3PW91 than GGA+U, see Figs. 4 and 5. This implies that the degree of localization is predicted to be less (more) by B3PW91 than by GGA+U (PBE-GGA), as discussed in our recent report⁶. The $DOS^{tot}(E_F)$ is affected by the degree of localization. In fact, like the effects of pressure on the value of the DOS at Fermi level, the total $DOS^{tot}(E_F)$ decreases as the degree

of localization increases, but the effect of localization degree is more than the that of pressure. The value of total $DOS(E_F)$ is predicted to be the highest (lowest) by PBE-GGA (GGA+U) with the lowest (highest) degree of localization among the three considered functionals, see Table 2 as tabulated in the main manuscript.

Thus from the above observations in our theoretical study we can conclude that the pressure cannot but localization degree can considerably change the electronic structures of the strongly correlated CeRhIn₅ compound. We know that in experiment, however, the pressure can also remarkably change the properties of this system. This is so, because when we apply pressure experimentally, the localization of the system is also naturally changed in strongly correlated systems. But, in contrast to the experiment, when we apply pressure theoretically the degree of localization is not changed automatically. This is so, because in the current available theoretical approaches the degree of localization should be applied manually by selecting an appropriate functional. In other words, in the current theoretical schemes, the localization degree has not been related to the pressure because of the complicated nature of such a case-dependent relation. But, in experiment they are naturally related to each other. Therefore, in theory one should case by case consider a suitable degree of localization for every pressure⁶.

Two Fortran programs are presented below based on the flowchart presented in Fig. 6. The names of these programs are max_con and max_pf. They are used for extracting the maximum values of the thermoelectric parameters from the "CeRhIn5.condtens" file. This file is as an output of the BoltzTrap code. The BoltzTrap code itself uses some of the output files of the WIEN2k code as its inputs to produce "CeRhIn5.condtens" file. The "CeRhIn5.condtens" is an input file for max_con and max_pf. The max_con program is written to find the maximum values of hole-like and electron-like of Seebeck coefficient, maximum values of electrical and thermal conductivities. The second program is used for finding the maximum values of the power factor and electronic figure of merit (Z) along a and c crystalline axes as well as the chemical potential and doping levels related to these maximums form "CeRhIn5.condtens" file for CeRhIn₅ compound. The range of doping level in these programs is optional and can be controlled in max_con and max_pf programs.

3.1 Program max_con

This program calculates the maximum values of hole like Seebeck coefficient along the a axis (smaxxx_s), and along the c axis (smaxzz_s), electron like Seebeck coefficient along the a axis (sminxx_s), and along the c axis (sminzz_s), electrical conductivity along the a axis (sig_maxxx), electrical conductivity along the c axis (sig_maxzz), thermal conductivity along the a axis (kapp_maxxx), thermal conductivity along the c axis (kapp_maxzz).

```
character*20 :: title, filename, input_file
real*8, allocatable :: a(:, :)
real*8 Tmax, smaxxx_s, sminxx_s, smaxzz_s, sminzz_s,
    imaxxx_s, iminxx_s, imaxzz_s, iminzz_s,
sig_maxxx, sig_maxzz, imaxxx_sig, imaxzz_sig,
    kapp_maxxx, kapp_maxzz, imaxxx_kapp, imaxzz_kapp
integer b
```

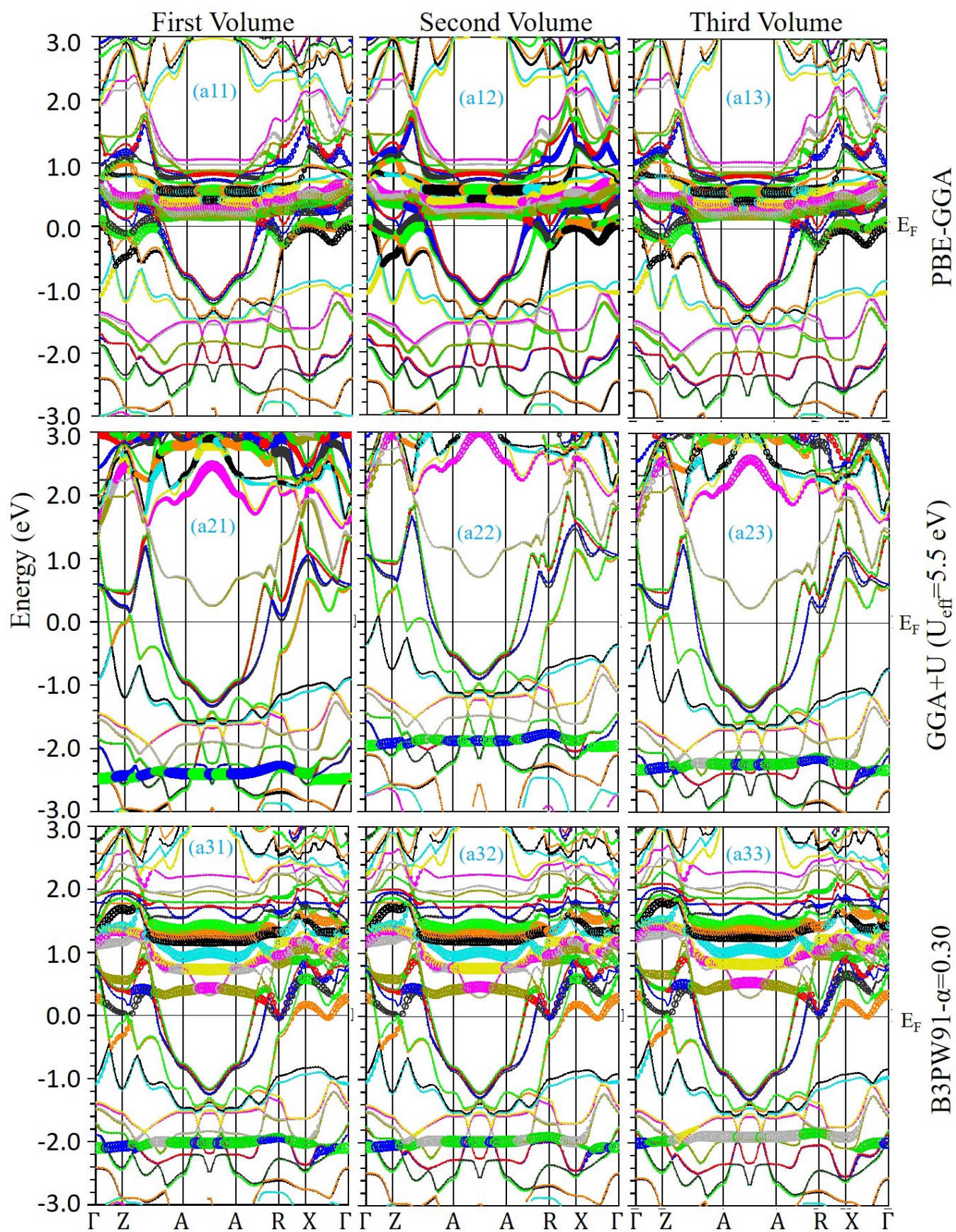



Fig. 2 Band structure of CeRhIn₅ for spin up direction utilizing a variety of XCFs in various volumes of CeRhIn₅ compound. The first volume is selected to be the experimental volume at zero pressure and the second (third) volume is 2% (5%) smaller than the first volume.

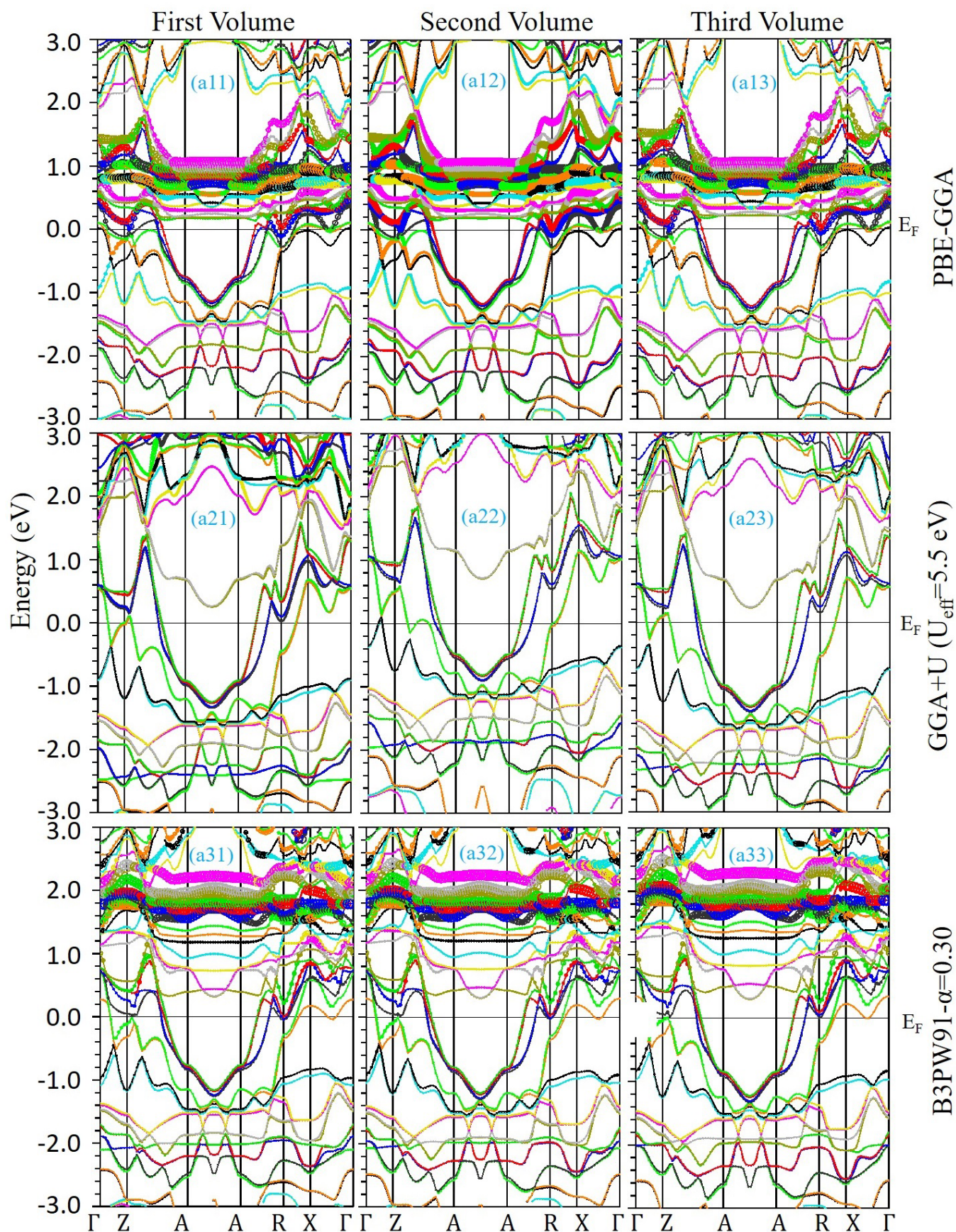


Fig. 3 Band structure of CeRhIn₅ for spin down direction utilizing a variety of XCFs in various volumes of CeRhIn₅ compound. The first volume is selected to be the experimental volume at zero pressure and the second (third) volume is 2% (5%) smaller than the first volume.

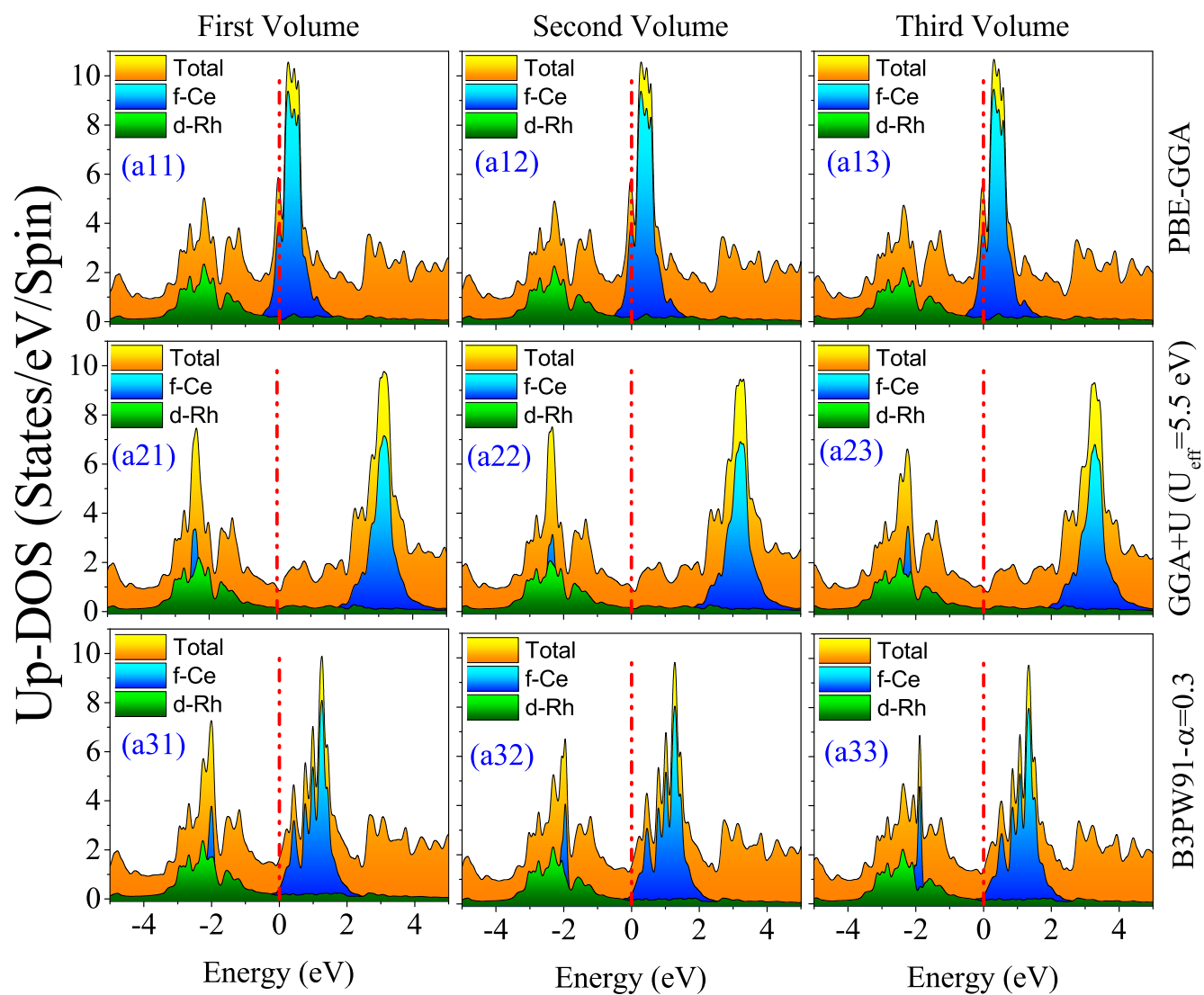


Fig. 4 Total as well as partial 4f-Ce and 4d-Rh DOSs of CeRhIn₅ for spin up using various XCFs for three different volumes of CeRhIn₅ compound. The first volume corresponds to the experimental volume at zero pressure. The second and third volumes are 2% and 5% smaller than the first volume, respectively.

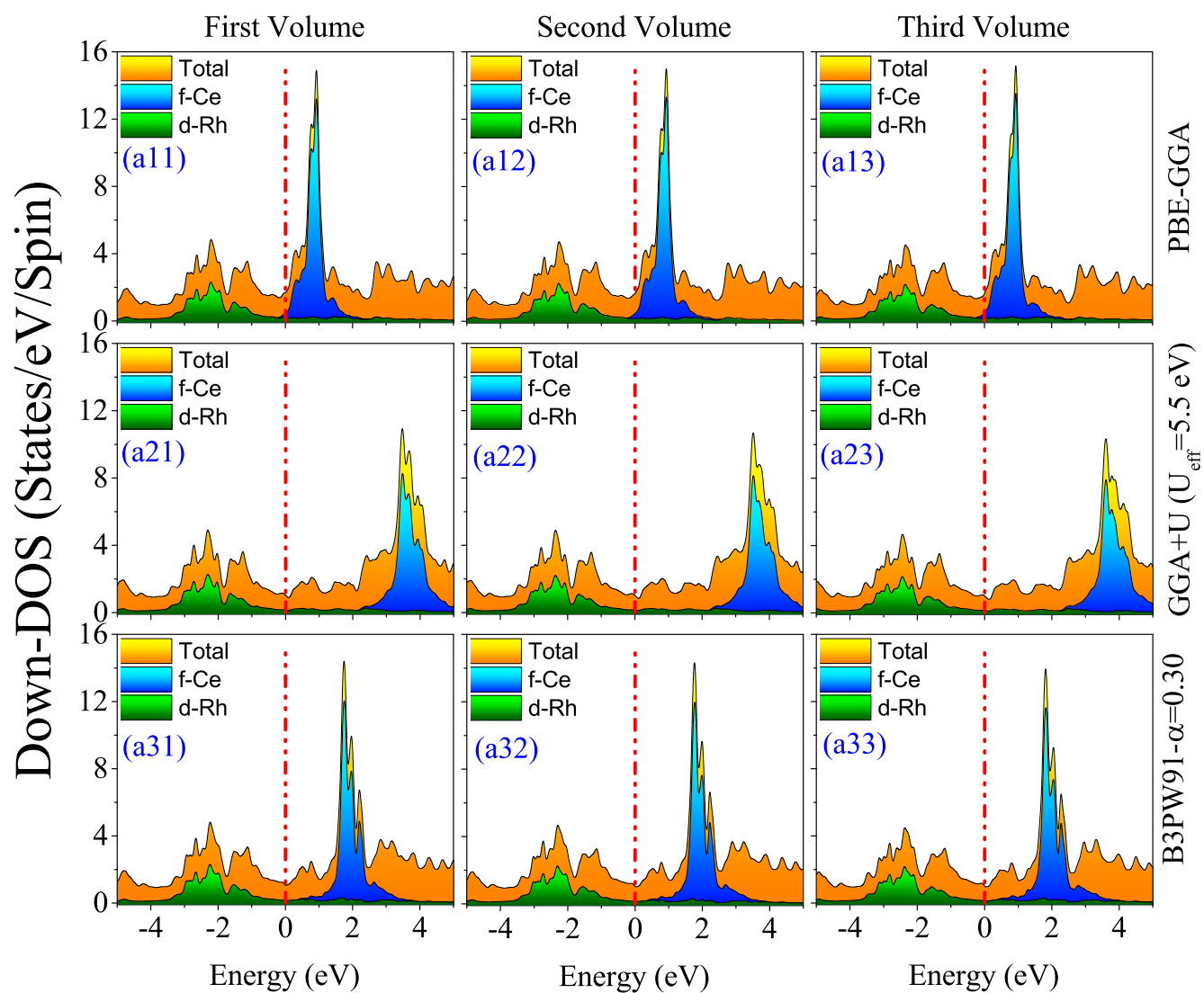


Fig. 5 Total as well as partial 4f-Ce and 4d-Rh DOSs of CeRhIn₅ for spin down using various XCFs for three different volumes of CeRhIn₅ compound. The first volume corresponds to the experimental volume at zero pressure. The second and third volumes are 2% and 5% smaller than the first volume, respectively.

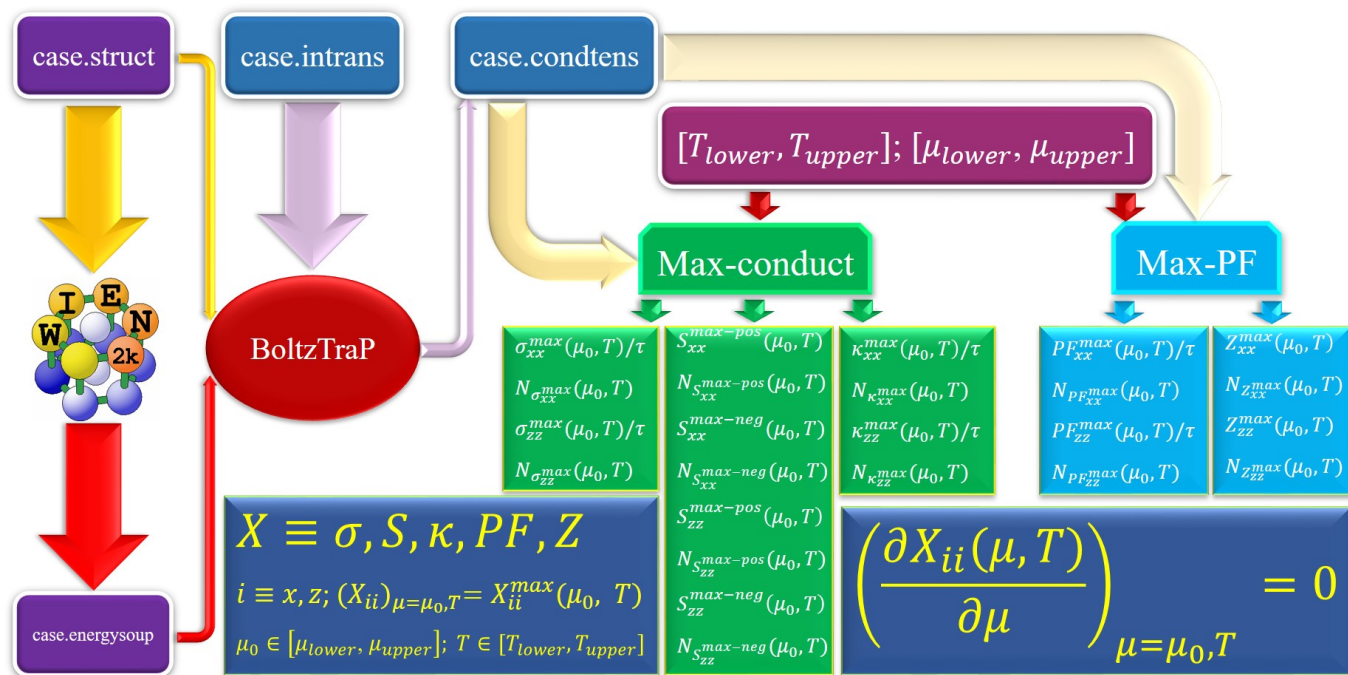


Fig. 6 Flowchart of the tasks performed to represent the thermoelectric results reported in this work.

```

print*, "Input file name?"
read*, filename
input_file = trim(filename) // '.condtens'
print*, 'Tmax?'
read*, Tmax
print*, "Minimum value for doping level (1/cm^3)?" !
    At this line the user determines the minimum of
    doping level in carrier/cm^3 unit
read*, Doplev_min
print*, "Maximum value for doping level (1/cm^3)?" !
    At this line the user determines the maximum of
    doping level carrier/cm^3 unit
read*, Doplev_max
print*, "Volume of system (a.u.^3)?" !At this line the
    user determines the volume of system in a.u.^3
    unit
read*, Vol
Vol=Vol*(0.148187e-24) ! the unit of volume is
    calculated in cm^3 unit
Doplev_min = Doplev_min*Vol ! the minimum of doping
    level is calculated in carrier/uc unit
Doplev_max = Doplev_max*Vol ! the maximum of doping
    level is calculated in carrier/uc unit
print*, Vol, Doplev_min, Doplev_max ! the volume in
    cm^3 unit, and the minimum and maximum of
    doping level in carrier/uc are printed to check by
    user
open(2, file = input_file)
b = -1
do while (io /= -1)
    read(2,*, iostat=io)
    b=b+1
end do
print*, b
allocate (a(b,30))
close(2)
io = 0

```

```

open(3,file='output_s') ! Output file includes
    temperature, maximum values of hole and electron
    like
Seebeck coefficients along both a and c axes, the
    chemical potential and the doping level related
    to these
maximum values.
open(4,file = 'output_sig') ! Output file includes
    temperature, maximum values of electrical
    conductivities along both a and c axes, the chemical
    potential and the doping level related to these
    maximum values.
open(14, file = 'output_kap') ! Output file includes
    temperature, maximum values of thermal
    conductivities along both a and c axes, the chemical
    potential and the doping level related to these
    maximum values.

ti = 0
1000 ti = ti + 1
    smaxxx = -1
    imaxxx_s = 0
    smaxzz = 0
    imaxzz_s = 0
    sminxx = 0
    iminxx_s = 0
    sminzz = 0
    iminzz_s = 0
    sig_maxxxx = 0
    imaxxx_sig = 0
    sig_maxzz = 0
    imaxzz_sig = 0
    kapp_maxxxx = 0
    imaxxx_kapp = 0
    kapp_maxzz = 0
    imaxzz_kapp = 0
    io = 0
open(2, file=input_file)

```



```

read(2, *) title
do i = 1, b-1
  read (2, *) (a(i, j), j = 1, 30)
  if (a(i, 2) == ti) then
    if (a(i, 3) <= Doplev_max .And. a(i,3) >
      = Doplev_min) then !This line limits
      the doping levels of maximum
      thermoelectric parameters.
#####
!This section of program calculates the hole and
electron like of Seebeck coefficient along the a
axis, i.e., smaxxx and sminxx, as well as the row
number of these values, i.e., imaxxx_s and
iminxx_s, respectively at ti temperature.

if (a(i,13) > smaxxx) then
  smaxxx=a(i,13)
  imaxxx_s=i
end if
if (a(i,13)<sminxx) then
  sminxx=a(i,13)
  iminxx_s=i
end if
#####
!This section of program calculates the maximum
values of hole and electron like of Seebeck
coefficient along the c axis, i.e., smaxzz and
sminzz, as well as the row number of these values
, i.e., imaxzz_s and iminzz_s, respectively at ti
temperature

if (a(i, 21) > smaxzz) then
  smaxzz = a(i, 21)
  imaxzz_s = i
end if
if (a(i, 21) < sminzz) then
  sminzz = a(i, 21)
  iminzz_s = i
end if
#####
!This section of program calculates the maximum value
of electrical conductivity along the a (
sig_maxxx) and c axes (sig_maxzz), as well as the
row number of these values, i.e imaxxx_sig and
imaxzz_sig, respectively at ti temperature
if (a(i, 4) > sig_maxxx) then
  sig_maxxx = a(i, 4)
  imaxxx_sig = i
end if
if (a(i,12) > sig_maxzz) then
  sig_maxzz = a(i,12)
  imaxzz_sig = i
end if
#####
!This section of program calculates the maximum value
of thermal conductivity along the a (kapp_maxxx)
and c axes (kapp_maxzz), as well as the row
number of these values, i.e imaxxx_kapp and
imaxzz_kapp, respectively at ti temperature
if (a(i, 22) > kapp_maxxx) then
  kapp_maxxx = a(i, 22)
  imaxxx_kapp = i
end if
if (a(i, 30) > kapp_maxzz) then
  kapp_maxzz = a(i,30)
  imaxzz_kapp = i
end if

```

```

end if
end if
#####
write(3,200) ti, a(imaxxx_s,1), a(imaxxx_s,3), a(
  imaxxx_s,13), a(iminxx_s,1), a(iminxx_s,3), a(
  iminxx_s,13), a(imaxzz_s,1), a(imaxzz_s,3), a(
  imaxzz_s,21), a(iminzz_s,1), a(iminzz_s,3), a(
  iminzz_s,21)
200 format(f10.4,4(1x, f10.4, 1x, f15.8, 1x, e15.8)
)
  write(4,100) ti, a(imaxxx_sig,1), a(imaxxx_sig
    ,3), a(imaxxx_sig,4), a(imaxzz_sig,1), a(
    imaxzz_sig,3), a(imaxzz_sig,12)
  write(14,100) ti, a(imaxxx_kapp,1), a(
    imaxxx_kapp,3), a(imaxxx_kapp,22), a(
    imaxzz_kapp,1), a(imaxzz_kapp,3), a(
    imaxzz_kapp,30)
100 format(f10.4,2(1x,f10.4,1x,f15.8,1x,e15.8))
  close (2)
  if (ti<Tmax) then
    goto 1000
  end if
\end
#####

```

3.2 Program max_pf

This program calculates the maximum values of power factor along the a (PF_maxxx) and c axes (PF_maxzz), the maximum values of electronic figure of merit along the a (ZT_maxxx) and c axes (ZT_maxzz)

```

character*20 :: title, filename, input_file
real*8, allocatable :: a(:,,:), con(:,,:), seeb
(:,,:), seeb2(:,,:), PF(:,,:), c(:,,:), ZT(:,,:), d
(:,,:)
real*8 Tmax, PF_maxxx, PF_maxzz, imaxxx_PF,
  imaxzz_PF, ti, ZT_maxxx, ZT_maxzz,
  imaxxx_ZT,
  imaxzz_ZT, Doplev_min, Doplev_max, Vol
integer b
print*, "Input file name?"
read*, filename
input_file=trim(filename) // '.condtens'
print*, 'Tmax?'
read*, Tmax
print*, "Minimum value for doping level (1/cm
  ^3)?"
read*, Doplev_min
rint*, "Maximum value for doping level (1/cm^3)
  ?"
read*, Doplev_max
print*, "Volume of system (a.u^3)?"
read*, Vol
Vol=Vol*(0.148187e-24)
Doplev_min=Doplev_min*Vol
Doplev_max=Doplev_max*Vol
print*, Vol, Doplev_min, Doplev_max
open(12, file=input_file)
b=-1
do while (io /= -1)
  read(12,*, iostat=io)
  b=b+1
end do
close(12)
io=0

```

```

print*, b
allocate (a(b,30))
allocate (seeb(3,3))
allocate (con(3,3))
allocate (seeb2(3,3))
allocate (PF(b-1,6))
allocate (ZT(b-1,6))
open(12, file=input_file)
open(13, file='con')
open(14, file='seeb')
open(15, file='seeb2')
open(16, file='PF')
open(17, file='ZT')
read(12,*) title
do i=1, b-1
  read (12,*) (a(i,j),j=1,30)
  m=4
  n=13
#####
!This section calculates the square of Seebeck
coefficient tensor (S^2).
  do k=1,3
    do l=1,3
      con(k,l)=a(i, m)
      Seeb(k,l)=a(i, n)
      m=m+1
      n=n+1
      write(13,*) con(k, l)
      write(14,*) seeb(k, l)
    end do
  end do

  do p=1,3
    do k=1,3
      seeb2(p, k)=0
      do l=1, 3
        seeb2(p,k)=seeb2(p,k)+seeb(p,
          l)*seeb(l,k)
      end do
      write(15,*) seeb2(p,k)
    end do
  end do
#####
! This section calculates the diagonal elements of
power factor.
  PF(1, 1) = seeb2(1, 1)*con(1, 1) + seeb2(1, 2)*
    con(2, 1) + seeb2(1, 3)*con(3, 1)
  PF(1, 2) = seeb2(2, 1)*con(1, 2) + seeb2(2, 2)*
    con(2, 2) + seeb2(2, 3)*con(3, 2)
  PF(1, 3) = seeb2(3, 1)*con(1, 3) + seeb2(3, 2)*
    con(2, 3) + seeb2(3, 3)*con(3, 3)
  write(16,*) a(i,1),a(i,2),a(i,3), PF(1,1), PF
    (1,2),PF(1,3)
#####
! This section calculates the diagonal elements of
electronic figure of merit.
  ZT(1, 1) = PF(1, 1)/a(i, 22)
  ZT(1, 2) = PF(1, 2)/a(i, 26)
  ZT(1, 3) = PF(1, 3)/a(i, 30)
  write(17, *) a(i, 1), a(i, 2), a(i, 3), ZT(1,
    1), ZT(1, 2), ZT(1, 3)
end do
close(16)
close (17)
#####
! This section calculates the maximum values of power
factor along the a (PF_maxxx) and c (PF_maxzz)
axes at temperature ti.

open(18, file = 'PF-max')
open(19, file = 'ZT-max')
ti=0
allocate(c(b-1,6))
allocate(d(b-1,6))
1000 ti=ti+1
  PF_maxxx = 0
  PF_maxzz = 0
  imaxxx_PF = 0
  imaxzz_PF = 0
  open(16, file = 'PF')
  do i=1, b-1
    read(16,*) (c(i,j), j=1,6)
    if (c(i,2) == ti) then
      if (a(i, 3) <= Doplev_max .
        And. a(i, 3) >=
        Doplev_min) then
        if (c(i,4) > PF_maxxx)
          then
            PF_maxxx = c(i,
              4)
            imaxxx_PF = i
          end if
        if (c(i, 6) > PF_maxzz)
          then
            PF_maxzz = c(i,
              6)
            imaxzz_PF=i
          end if
        end if
      end if
    end do
#####
! This section calculates the maximum values of
electronic figure of merit along the a (ZT_maxxx)
and c (ZT_maxzz) axes at temperature ti.
  ZT_maxxx = 0
  ZT_maxzz = 0
  imaxxx_ZT = 0
  imaxzz_ZT = 0
  open(17, file = 'ZT')
  do i=1, b-1
    read(17, *) (d(i, j), j = 1, 6)
    if (d(i, 2) == ti) then
      if (a(i,3) <= Doplev_max .And. a(i
        ,3) >= Doplev_min) then
        if (d(i, 4) > ZT_maxxx) then
          ZT_maxxx = d(i, 4)
          imaxxx_ZT = i
        end if
        if (d(i, 6) > ZT_maxzz) then
          ZT_maxzz = d(i, 6)
          imaxzz_ZT = i
        end if
      end if
    end if
  end do
#####
100 format (f10.4, 1x, f10.4, 1x,f10.4, e15.8, 1x,
  f10.4, 1x, f10.4, e15.8)
  write(18, 100) ti, c(imaxxx_PF, 1), c(
    imaxxx_PF, 3), PF_maxxx, c(imaxzz_PF,
    1), c(imaxzz_PF, 3),
    PF_maxzz
  write(19, 100) ti, c(imaxxx_ZT, 1), c(imaxxx_ZT
    , 3), ZT_maxxx, c(imaxzz_ZT, 1),c(imaxzz_ZT
    , 3),

```



```

ZT_maxzz
close (16)
close (17)
if (ti<Tmax) then
    goto 1000
end if
end
#####

```

References

- 1 R. T. Macaluso, J. Sarrao, P. Pagliuso, N. Moreno, R. Goodrich, D. Browne, F. R. Fronczek and J. Y. Chan, *Journal of Solid State Chemistry*, 2002, **166**, 245 – 250.
- 2 E. Moshopoulou, Z. Fisk, J. Sarrao and J. Thompson, *Journal of Solid State Chemistry*, 2001, **158**, 25 – 33.
- 3 E. Moshopoulou, J. Sarrao, P. Pagliuso, N. Moreno, J. Thompson, Z. Fisk and R. Ibberson, *Applied Physics A*, 2002, **74**, s895–s897.
- 4 M. Gamża, A. Żlebarski and J. Deniszczyk, *Journal of Physics: Condensed Matter*, 2008, **20**, 115202.
- 5 S. Jalali Asadabadi, *Phys. Rev. B*, 2007, **75**, 205130.
- 6 M. Yazdani-Kachoei, S. Jalali-Asadabadi, I. Ahmad and K. Zarringhalam, *Scientific Reports*, 2016, **6**, 31734.