# Bandstructure of κ-(BEDT-TTF)2Cu(NCS)2
# Harukazu YOSHINO, April 22, 2010

In[1]:=

```
<< "VectorAnalysis`"
```

In[2]:=

```
Off[General::"spell1"]
```

In[3]:=

```
(* Date and time for record *)
timeStart = DateList[]
```

Out[3]=

```
{2010, 4, 22, 14, 37, 3.5964463}
```

---

## Solving the Secular Equation

In[4]:=

```
(* Lefthand side of the secular equation *)
    H = {{h11, h12, h13, h14},
        {h21, h22, h23, h24},
        {h31, h32, h33, h34},
     {h41, h42, h43, h44}}
```

Out[4]=

```
{{h11, h12, h13, h14}, {h21, h22, h23, h24}, {h31, h32, h33, h34}, {h41, h42, h43, h44}}
```

In[5]:=

```
(* Diagonal elements of the 4 x 4 matrix *)
h11 = -ene; h22 = h11; h33 = h11; h44 = h11
```

Out[5]=

```
-ene
```

In[6]:=

```
(* Determinant of the matrix *)
J0 = Simplify[Det[H]]
```

Out[6]=

$$ene^4 + h14\,h23\,h32\,h41 - h13\,h24\,h32\,h41 - h12\,h23\,h34\,h41 - h14\,h23\,h31\,h42 + h13\,h24\,h31\,h42 - h13\,h21\,h34\,h42 - h12\,h24\,h31\,h43 - h14\,h21\,h32\,h43 + h12\,h21\,h34\,h43 - ene\,(h12\,h23\,h31 + h13\,h21\,h32 + h12\,h24\,h41 + h13\,h34\,h41 + h14\,h21\,h42 + h23\,h34\,h42 + h14\,h31\,h43 + h24\,h32\,h43) - ene^2\,(h12\,h21 + h13\,h31 + h23\,h32 + h14\,h41 + h24\,h42 + h34\,h43)$$

In[7]:=

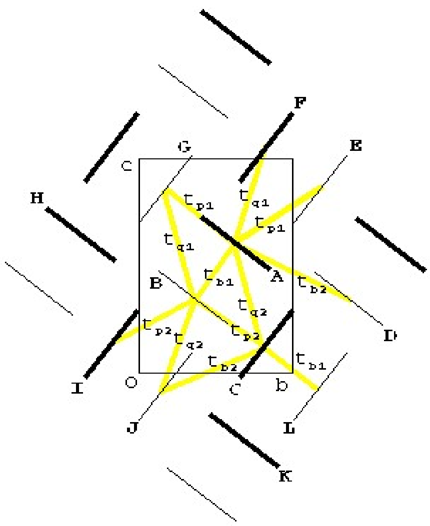
```
(* Offdiagonal elements of the matrix  Refs.1,2 *)
h12 = Exp[I k.ab] Bab + Exp[I k.ad] Bad;
h21 = h12 /. I -> -I;
h13 = Exp[I k.ac] Bac + Exp[I k.af] Baf;
h31 = h13 /. I -> -I;
h14 = Exp[I k.ae] Bae + Exp[I k.ag] Bag;
h41 = h14 /. I -> -I;
h23 = Exp[I k.bc] Bbc + Exp[I k.bi] Bbi;
h32 = h23 /. I -> -I;
h24 = Exp[I k.bg] Bbg + Exp[I k.bj] Bbj;
h42 = h24 /. I -> -I;
h34 = Exp[I k.cl] Bcl + Exp[I k.cj] Bcj;
h43 = h34 /. I -> -I;
```

In[19]:=

```
(* Positional vectors of each BEDT-TTF molecule   Refs.1.2 *)
(* Vector ab is defined to be (2r, 2s) *)
oa = {(1/2) b + r, (1/2) c + s};
ob = {(1/2) b - r, (1/2) c - s};
oc = {b - r, s};
od = {(3/2) b - r, (1/2) c - s};
oe = {b + r, c - s};
of = {b - r, c + s};
og = {r, c - s};
oi = {-r, s};
oj = {r, -s};
ol = {b + r, -s};
```

In[29]:=

```
(* Relative vectors between neighbouring molecules *)
ab = ob - oa;
ad = od - oa;
ac = oc - oa;
af = of - oa;
ae = oe - oa;
ag = og - oa;
bc = oc - ob;
bi = oi - ob;
bg = og - ob;
bj = oj - ob;
cl = ol - oc;
cj = oj - oc;
```




or  A - L : BEDT-TTF

$t_{b1}, t_{b2}, t_{p1}, t_{p2}, t_{q1}, t_{q2}$
: transfer integrals

In[41]:=

```
(* Transfer integrals between neighbouring molecules   Ref.3 *)
Bab = tb1; Bcl = tb1;
Bae = tp1; Bag = tp1;
Bbc = tp2; Bbi = tp2;
Baf = tq1; Bbg = tq1;
Bac = tq2; Bbj = tq2;
Bad = tb2;
Bcj = tb2;
```

In[47]:=

```
(* k-vector *)
k = {kb, kc}
```

Out[47]=

```
{kb, kc}
```

In[48]:=

```
(* Expand and simplify the determinant, J *)
J0 = ComplexExpand[J0];
```

In[49]:=

```
J0 = FullSimplify[Collect[TrigExpand[Simplify[J0]], ene]]
```

Out[49]=

$$\mathrm{ene}^4+\mathrm{tb1}^4+4\,\mathrm{tb1}^2\,\mathrm{tb2}^2+\mathrm{tb2}^4+6\,\mathrm{tp1}^2\,\mathrm{tp2}^2-4\,\mathrm{tb1}\,\mathrm{tb2}\,\mathrm{tq1}^2+\mathrm{tq1}^4-8\,\mathrm{tp1}\,\mathrm{tp2}\,\mathrm{tq1}\,\mathrm{tq2}-4\,\mathrm{tb1}\,\mathrm{tb2}\,\mathrm{tq2}^2+4\,\mathrm{tq1}^2\,\mathrm{tq2}^2+\mathrm{tq2}^4-2\,\mathrm{ene}^2\left(\mathrm{tb1}^2+\mathrm{tb2}^2+\mathrm{tp1}^2+\mathrm{tp2}^2+\mathrm{tq1}^2+\mathrm{tq2}^2\right)-8\,\mathrm{ene}\,(\mathrm{tb1}+\mathrm{tb2})\,\mathrm{Cos}\left[\frac{\mathrm{b\,kb}}{2}\right]^2\left(\mathrm{tp1}\,\mathrm{tq1}+\mathrm{tp2}\,\mathrm{tq2}+(\mathrm{tp2}\,\mathrm{tq1}+\mathrm{tp1}\,\mathrm{tq2})\,\mathrm{Cos}[\mathrm{c\,kc}]\right)+2\Big(\left(\mathrm{tb1}^2\,\mathrm{tb2}^2+\mathrm{tp1}^2\,\mathrm{tp2}^2\right)\mathrm{Cos}[2\,\mathrm{b\,kb}]-2\left(\mathrm{tp1}\,\mathrm{tp2}\left(\mathrm{tb1}^2+\mathrm{tb1}\,\mathrm{tb2}+\mathrm{tb2}^2+\mathrm{tq1}^2\right)+\mathrm{tq1}\left(\mathrm{ene}^2+2\,\mathrm{tb1}\,\mathrm{tb2}-\mathrm{tq1}^2\right)\mathrm{tq2}+\mathrm{tp1}\,\mathrm{tp2}\,\mathrm{tq2}^2-\mathrm{tq1}\,\mathrm{tq2}^3+\mathrm{tb1}\,\mathrm{tb2}\,\mathrm{tp1}\,\mathrm{tp2}\,\mathrm{Cos}[2\,\mathrm{b\,kb}]\right)\mathrm{Cos}[\mathrm{c\,kc}]+\mathrm{Cos}[\mathrm{b\,kb}]\Big(4\,\mathrm{tp1}^2\,\mathrm{tp2}^2-\mathrm{ene}^2\left(2\,\mathrm{tb1}\,\mathrm{tb2}+\mathrm{tp1}^2+\mathrm{tp2}^2\right)+\left(\mathrm{tb1}^2+\mathrm{tb2}^2\right)\left(2\,\mathrm{tb1}\,\mathrm{tb2}-\mathrm{tq1}^2\right)-4\,\mathrm{tp1}\,\mathrm{tp2}\,\mathrm{tq1}\,\mathrm{tq2}-\left(\mathrm{tb1}^2+\mathrm{tb2}^2\right)\mathrm{tq2}^2-2\left(\mathrm{tp1}\,\mathrm{tp2}\left((\mathrm{tb1}+\mathrm{tb2})^2+\mathrm{tq1}^2\right)+\left(\mathrm{tb1}^2+\mathrm{tb2}^2\right)\mathrm{tq1}\,\mathrm{tq2}+\mathrm{tp1}\,\mathrm{tp2}\,\mathrm{tq2}^2\right)\mathrm{Cos}[\mathrm{c\,kc}]\Big)+\mathrm{tq1}^2\,\mathrm{tq2}^2\,\mathrm{Cos}[2\,\mathrm{c\,kc}]\Big)$$

In[50]:=

```
(* Replace characters of transferintegrals with number in meV *)
J = J0 /. {tb1 -> -257., tb2 -> -105., tp1 -> -114., tp2 -> -100., tq1 -> 17., tq2 -> 29.}
```

Out[50]=

$$8.01137\times10^9-202\,400.\,\mathrm{ene}^2+\mathrm{ene}^4+2896.\,\mathrm{ene}\,\mathrm{Cos}\left[\frac{\mathrm{b\,kb}}{2}\right]^2(-4838.-5006.\,\mathrm{Cos}[\mathrm{c\,kc}])+2\Big(8.5815\times10^8\,\mathrm{Cos}[2\,\mathrm{b\,kb}]+\mathrm{Cos}[\mathrm{b\,kb}]\left(4.56995\times10^9-76\,966.\,\mathrm{ene}^2-3.08956\times10^9\,\mathrm{Cos}[\mathrm{c\,kc}]\right)-2\left(1.19874\times10^9+493.\left(53\,681.+\mathrm{ene}^2\right)+3.07629\times10^8\,\mathrm{Cos}[2\,\mathrm{b\,kb}]\right)\mathrm{Cos}[\mathrm{c\,kc}]+243\,049.\,\mathrm{Cos}[2\,\mathrm{c\,kc}]\Big)$$

In[51]:=

```
(* Replace b kb and c kc with theta and phi for simplicity *)
J = J /. {b kb -> theta, c kc -> phi}
```

Out[51]=

$$8.01137\times10^9-202\,400.\,\mathrm{ene}^2+\mathrm{ene}^4+2896.\,\mathrm{ene}\,(-4838.-5006.\,\mathrm{Cos}[\mathrm{phi}])\,\mathrm{Cos}\left[\frac{\mathrm{theta}}{2}\right]^2+2\Big(243\,049.\,\mathrm{Cos}[2\,\mathrm{phi}]+\left(4.56995\times10^9-76\,966.\,\mathrm{ene}^2-3.08956\times10^9\,\mathrm{Cos}[\mathrm{phi}]\right)\mathrm{Cos}[\mathrm{theta}]+8.5815\times10^8\,\mathrm{Cos}[2\,\mathrm{theta}]-2\,\mathrm{Cos}[\mathrm{phi}]\left(1.19874\times10^9+493.\left(53\,681.+\mathrm{ene}^2\right)+3.07629\times10^8\,\mathrm{Cos}[2\,\mathrm{theta}]\right)\Big)$$

In[52]:=

```
(* Solve the equation *)
solution = Solve[J == 0, ene];
```

In[53]:=

```
(* Define the 4 bands using the above solution *)
kappa1 = ene /. solution[[1]][[1]];
kappa2 = ene /. solution[[2]][[1]];
kappa3 = ene /. solution[[3]][[1]];
kappa4 = ene /. solution[[4]][[1]];
```

In[57]:=

```
Chop[kappa1 /. {theta → -3.14159, phi → -1.15743}, 10^-5]
```

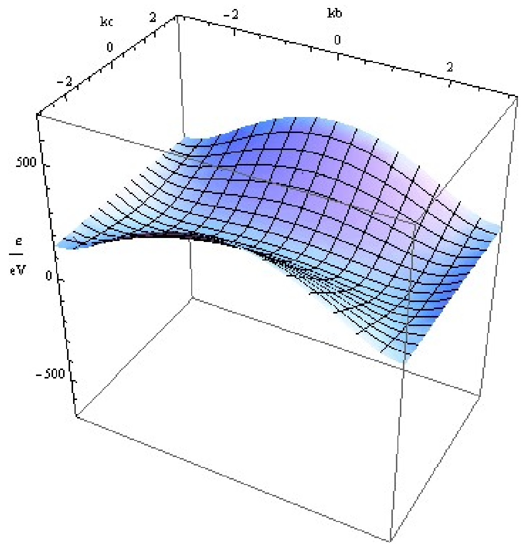
Out[57]=

```
156.939
```

In[58]:=

```
(* Band 1 *)
ParametricPlot3D[{theta, phi, kappa1}, {theta, -Pi, Pi}, {phi, -Pi, Pi}, BoxRatios -> {1, 8.440/13.124, 1},
PlotRange -> {{-Pi, Pi}, {-Pi, Pi}, {-700, 700}}, PlotPoints → 6,
 AxesLabel -> {kb, kc, E/eV}]
```

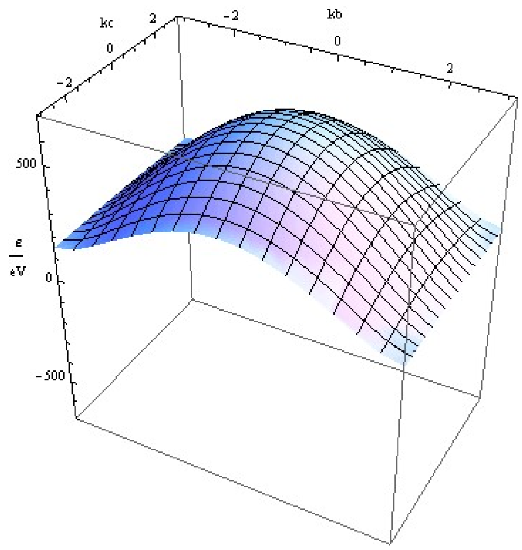
Out[58]=




In[59]:=

```
(* Band 2 *)
ParametricPlot3D[{theta, phi, kappa2}, {theta, -Pi, Pi}, {phi, -Pi, Pi}, BoxRatios -> {1, 8.440/13.124, 1},
PlotRange -> {{-Pi, Pi}, {-Pi, Pi}, {-700, 700}}, PlotPoints → 6,
 AxesLabel -> {kb, kc, E/eV}]
```

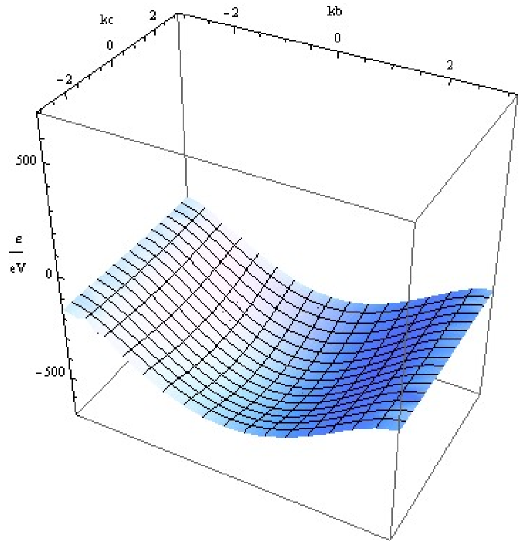
Out[59]=




In[60]:=

```
(* Band 3 *)
ParametricPlot3D[{theta, phi, kappa3}, {theta, -Pi, Pi}, {phi, -Pi, Pi}, BoxRatios -> {1, 8.440/13.124, 1},
PlotRange -> {{-Pi, Pi}, {-Pi, Pi}, {-700, 700}}, PlotPoints → 6,
 AxesLabel -> {kb, kc, E/eV}]
```

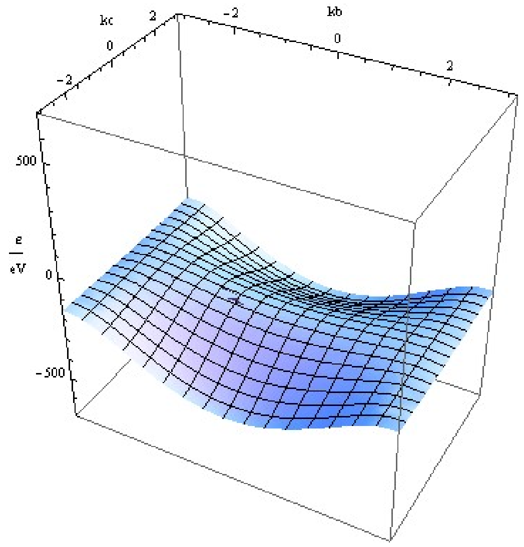
Out[60]=




In[61]:=

```
(* Band 4 *)
ParametricPlot3D[{theta, phi, kappa4}, {theta, -Pi, Pi}, {phi, -Pi, Pi}, BoxRatios -> {1, 8.440/13.124, 1},
PlotRange -> {{-Pi, Pi}, {-Pi, Pi}, {-700, 700}}, PlotPoints → 6,
 AxesLabel -> {kb, kc, E/eV}]
```

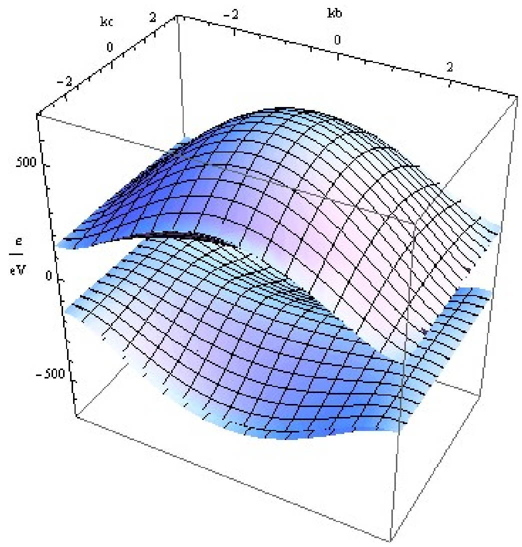
Out[61]=




In[62]:=

```
ParametricPlot3D[{{theta, phi, kappa1}, {theta, phi, kappa2}, {theta, phi, kappa3}, {theta, phi, kappa4}},
 {theta, -Pi, Pi}, {phi, -Pi, Pi}, BoxRatios -> {1, 8.440/13.124, 1}, PlotRange → {{-Pi, Pi}, {-Pi, Pi}, {-700, 700}},
 AxesLabel -> {kb, kc, E/eV}, PlotPoints → 6]
```

Out[62]=




## Calculate Fermi Energy

In[63]:=

```
band = {kappa1, kappa2};
```

- **Counting version**

In[64]:=

```
(* Division *)
nk = 7; (* increase this to get a finer value of Ef *)
div = 2^nk;
(* Cutoff *)
dSkCut = 10^-5;
(* Area to be calculated and 1st Burillouin zone *)
Sk = 0;
(* Change this if you want another filling, for example, 1/4-filled → 0.5, 1/2-filled→1, 3/4-filled→ 1.5 *)
SkF = 1;(* 1/2-filled of 2 bands = 3/4-filled of 4 bands *)

e1 = Chop[band[[1]] /. {theta → 0, phi → 0}, 10^-5]; (* Chop is needed to truncate small imaginary numbers. *)
e2 = Chop[band[[1]] /. {theta → Pi, phi → Pi}, 10^-5];
e3 = Chop[band[[2]] /. {theta → 0, phi → 0}, 10^-5];
e4 = Chop[band[[2]] /. {theta → Pi, phi → Pi}, 10^-5];
eneMin = Min[e1, e2, e3, e4];
eneMax = Max[e1, e2, e3, e4];
Ef1 = {eneMin, eneMax, (eneMin + eneMax) / 2}; (* Just to define the list *)
Sk1 = {0, 0, 0};(* Just to define the list *)

(* Make table of energy *)
eneB1 = Table[Chop[band[[1]] /. {theta → Pi / div * (i + .5), phi → Pi / div * (j + .5)}, 10^-5], {i, 0, div - 1}, {j, 0, div - 1}];
eneB2 = Table[Chop[band[[2]] /. {theta → Pi / div * (i + .5), phi → Pi / div * (j + .5)}, 10^-5], {i, 0, div - 1},
   {j, 0, 2 * div - 1}];

(* Find Ef of half filling for total of bands 1 and 2 *)
dSk = 1;
count2 = 0;
While[dSk > dSkCut && count2 < 30,
  count2++;
  (* Calculate three kinds of Sk *)
  Ef1[[3]] = (Ef1[[1]] + Ef1[[2]]) / 2;
  For[j = 1, j ≤ 3, j++,
   Sk1[[j]] = 0;
   Ef = Ef1[[j]];
   Sk = 0;
   For[p = 1, p <= div, p++,
    For[q = 1, q <= div, q++,
      (* Sk *)
      If[eneB1[[p]][[q]] ≤ Ef, Sk++];
      If[eneB2[[p]][[q]] ≤ Ef, Sk++];
     ];(* For(phi1) *)
   ]; (* For(theta1) *)
   Sk = Sk / (div^2);
   Sk1[[j]] = Sk - SkF; (* difference between calculated S and SF *)
  ]; (* For(j) *)
  Print["EF ", N[Ef1[[1]], 8], "  ", N[Ef1[[3]], 8], "  ", N[Ef1[[2]], 8], "  ",
   "Sk ", N[Sk1[[1]] + SkF, 8], "  ", N[Sk1[[3]] + SkF, 8], "  ", N[Sk1[[2]] + SkF, 8]];
  If[Sk1[[1]] * Sk1[[3]] < 0, Ef1[[2]] = Ef1[[3]], Ef1[[1]] = Ef1[[3]]];
  dSk = Abs[Sk1[[3]]];
 ];
(* While *)
Print["Ef=", Ef1[[3]], " meV"]
```

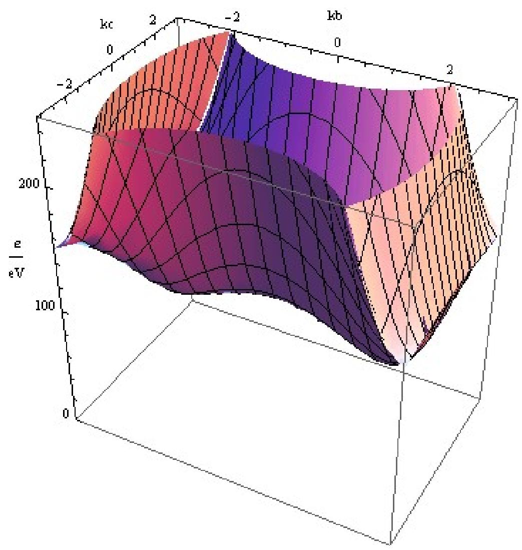
```
EF 102.31  362.275  622.24  Sk 0.13531494  1.3688354  2.0000000

EF 102.31  232.293  362.275  Sk 0.13531494  0.92901611  1.3688354

EF 232.293  297.284  362.275  Sk 0.92901611  1.1671753  1.3688354

EF 232.293  264.788  297.284  Sk 0.92901611  1.0541992  1.1671753

EF 232.293  248.54  264.788  Sk 0.92901611  0.99359131  1.0541992

EF 248.54  256.664  264.788  Sk 0.99359131  1.0239868  1.0541992
```

```
EF 248.54   252.602   256.664   Sk 0.99359131   1.0089111   1.0239868

EF 248.54   250.571   252.602   Sk 0.99359131   1.0010376   1.0089111

EF 248.54   249.556   250.571   Sk 0.99359131   0.99774170   1.0010376

EF 249.556   250.064   250.571   Sk 0.99774170   0.99945068   1.0010376

EF 250.064   250.317   250.571   Sk 0.99945068   1.0001831   1.0010376

EF 250.064   250.19   250.317   Sk 0.99945068   0.99969482   1.0001831

EF 250.19   250.254   250.317   Sk 0.99969482   0.99993896   1.0001831

EF 250.254   250.286   250.317   Sk 0.99993896   1.0000610   1.0001831

EF 250.254   250.27   250.286   Sk 0.99993896   0.99993896   1.0000610

EF 250.27   250.278   250.286   Sk 0.99993896   0.99993896   1.0000610

EF 250.278   250.282   250.286   Sk 0.99993896   0.99993896   1.0000610

EF 250.282   250.284   250.286   Sk 0.99993896   0.99993896   1.0000610

EF 250.284   250.285   250.286   Sk 0.99993896   1.0000000   1.0000610

Ef=250.285 meV
```

In[83]:=

```
ParametricPlot3D[{{theta, phi, kappa1}, {theta, phi, kappa2}}, {theta, -Pi, Pi}, {phi, -Pi, Pi},
 BoxRatios -> {1, 8.440 / 13.124, 1},
 AxesLabel -> {kb, kc, E / eV}, PlotPoints → 6,
 PlotRange -> {{-Pi, Pi}, {-Pi, Pi}, {0, Ef}}]
```

Out[83]=




In[84]:=

```
(* Date and time for record *)
timeEnd = DateList[];
timeEnd - timeStart
```

Out[85]=

```
{0, 0, 0, 0, 1, 7.1968435}
```

References


[1] H. Urayama, H. Yamochi, G. Saito, S. Sato, A. Kawamoto, J. Tanaka, T. Mori, Y. Maruyama and H. Inokuchi, Chem. Lett. (1988) 463.

[2] D. Jung, M. Evain, J. J. Nova, M.-H. Whangbo, M. A. Beno, A. M. Kini, A. J. Schultz, J. M. Williams and P. J. Nigrey, Inorg. Chem. **28** (1989) 4516.

[3] K. Oshima, T. Mori, H. Inokuchi, H. Urayama, H. Yamochi and G. Saito, Phys. Rev. B**38** (1988) 938.