Calculation of crystal field parameters and magnetism with Wannier functions Manual

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(Dated: January 5, 2017)

PACS numbers:
Keywords:

This is manual and documentation of CFP calculation. Illustration for $DyAlO_3$, $Dy_2Fe_2Si_2C$ (abbreviated to Dy) systems (inputs and outputs of the steps I - VI) is included in CFP_manual directory. The files needed are in subdirectory Nth_step/*case*; *case* $\equiv$ dyalo3 or Dy. For steps I and II consult WIEN2k user-guide. This manual refers to WIEN12k_14.1 user-guide, the example was calculated using WIEN2k_14.2.

Comparing to original version of the manual: 1st, 2nd, 3rd and 5th steps are unchanged, in 4th step program *bkq* was slightly modified to comply with the present version of $w2w$. 6th step - calculation of magnetism - was changed almost completely, not only the old programs were modified, but several new ones were added.

I. FIRST STEP: CALCULATION WITH f STATES IN CORE

This is standard WIEN2k non-spin-polarized calculation.
Start with init_lapw, but first case.struct must be created.
WIEN has several possibilities how to do it:

- using cif file
- using $w2web$
- modifying some of the examples in $SRC\_example\_struct\_files$

For the unit cell parameters we usually use experimental values, though WIEN can also be applied (user-guide sect. 5.3.1). Internal lattice parameters may be optimized (required in case of an impurity) using WIEN *mini* program (user-guide sect. 5.3.2). Atomic radius of R should be large, if possible $\sim$ 2.3-2.5 a.u.
With *case.struct*, the *case.inst* (input to the initial atomic program) is to be created by:
instgen
Proceed with
init_lapw
Usually we choose GGA for exchange-correlation potential (options 11, 13 or 19) and -6 Ry for energy to separate core and valence states. (in some cases this energy has to be increased). The following inputs created by init_lapw must be modified:

- in *case.in*1 (*case.in*2*c* in systems without the inversion symmetry, which leads to the complex eigenvectors) expansion energy of R(f) states must be put high $\sim$ 3 Ry, and step must be put equal to 0.
- in *case.inc* f states of R should be included containing actual number of f electrons and potential well $\sim$ 1 - 1.5 Ry inserted.
- in *case.in*2 (*case.in*2*c* in systems without the inversion symmetry) number of electrons must be reduced by actual number of R(f) electrons, which were put in the core. Also we increase as a rule $GMAX$ (last line) from 12 to 16.

When the *init_lapw* calculates k-list and the script ask you:
Shift of k-mesh allowed. Do you want to shift: (0=no, 1=shift)
enter 0.

Proceed with:
run_lapw -cc 0.00001 -p
cc charge convergence, p parallel execution. If the iteration procedure is after $\sim$ 20 steps not converging modify *case.inm*, changing $MSR1$ to $BROYD$ and use smaller mixing factor
Well converged results should be stored in separate directory e.g. $fcore$.

Results of this step are illustrated on Figs. 1 and 2.

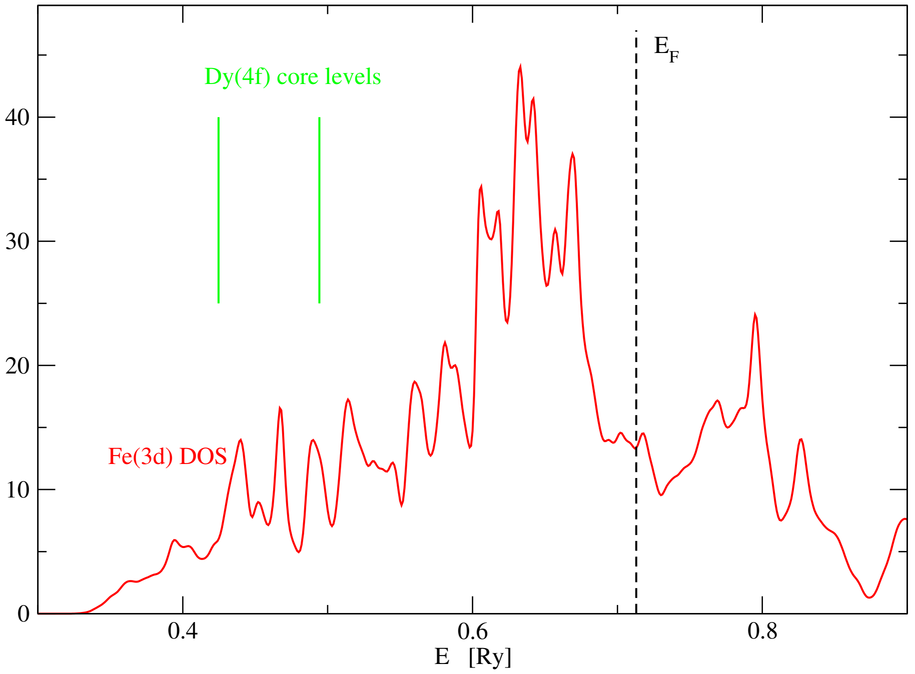

FIG. 1: $Dy_2Fe_2Si_2C$. Density of states projected on Fe(3d) states, Dy(4f) states were included in core.

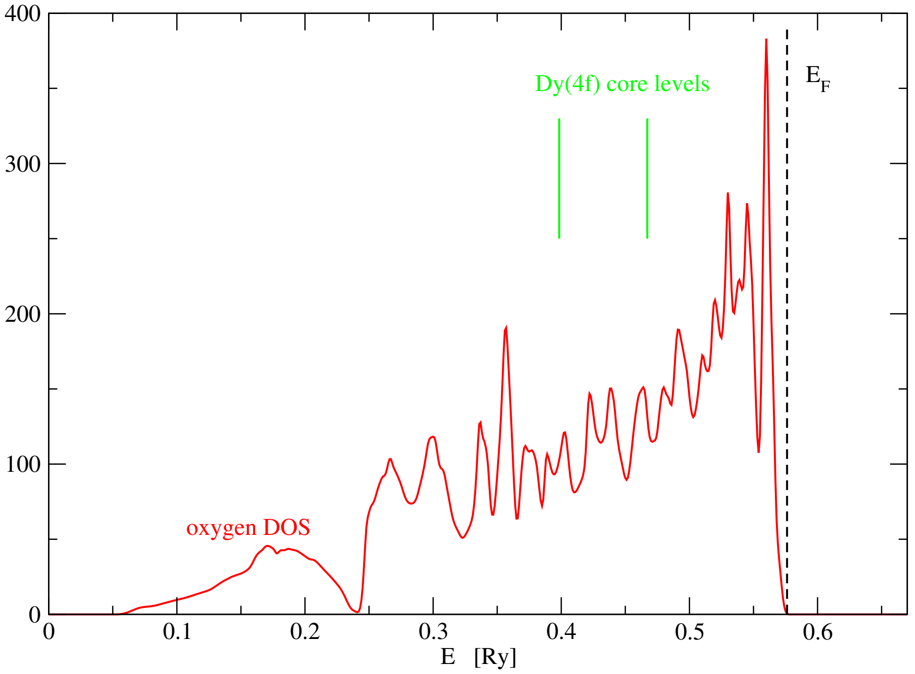

FIG. 2: $DyAlO_3$. Density of states projected on oxygen, Dy(4f) states were included in core.

II. SECOND STEP: f STATES INCLUDED IN VALENCE STATES

The valence states, which will be allowed to hybridize with R(f) should be selected. In oxides these states include as a rule oxygen $2p$ and $2s$, other states which might hybridize with R(f) could be added. Shift energy Δ for these selected states should be chosen (in oxide perovskites choosing Δ = -0.6 Ry for oxygen $2s$, $2p$ gave good results, in intermetallics $\Delta \simeq -0.4 - -0.2$ Ry seems to be appropriate, it is applied to the d states of transition metal). In accord with this selection orbital potential *case.vorb* should be created and *case.in*1 (*case.in*1*c* for systems without inversion) modified.

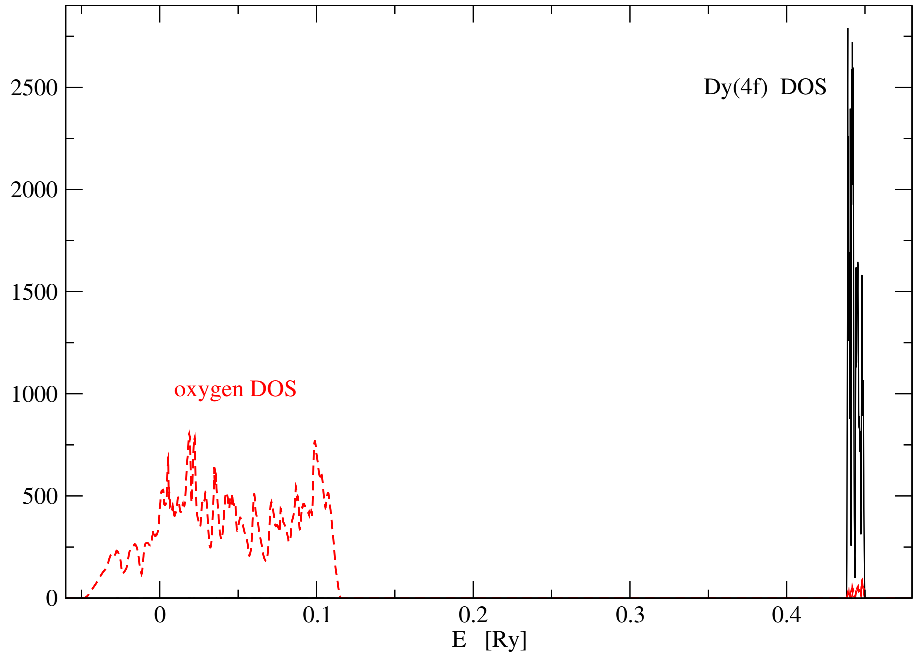

FIG. 3: $DyAlO_3$. Density of states projected on oxygen and on Dy(4f) states. Hybridization parameter Δ = -0.6 Ry.

- modification of $case.in1$ ($case.in1c$):
  - leave out all semi-core states like R($5s$, $5p$) etc.
  - For states selected as valence, put reasonable value for expansion energy (0.3 Ry for oxygen $2p$ and $2s$).
  - For f states expansion energy should be find out, as described below.
  - States which are not allowed to hybridize should have high expansion energy $\sim$ 3 Ry and step 0.
- orbital potential $case.vorb$
  orbital potential is a diagonal matrix and it should be created by hand.
  For selected valence states put Δ on the diagonal. It may be necessary to put large positive energy (e.g. 6 Ry) on diagonal elements of states which are not allowed to hybridize. To ease the construction of $case.vorb$ look in directory CFP_manual/2nd_step/vorb_help.

$w2w$ and $wannier90$ require the k-points in the whole Brillouin zone. To this end run
x kgen -fbz
Use the same division as in step I.
Finally run:
x lapw1 -orb (-p)

Find in the $lapw1$ output $case.scf1$ whether WIEN found the f states (it should be group of N_Rx7 closely spaced levels, where N_R is number of R ions) lying in the gap. If WIEN did not find f states or their energy is evidently false, change E_0, or/and change Δ. First ($Nmin$) and last ($Nmax$) index of f energies are needed for writing the input for $w2w$.

Results of this step are illustrated in Figs. 3 and 4.

III. THIRD STEP: w2w AND wannier90 CALCULATIONS

Proceed according to $w2w$ and $wannier90$ users-guides. Starting from WIEN2k_14.2 $w2w$ is contained in the WIEN2k release, $wannier90$ can be downloaded from
www.wannier.org
Start with writing input for $w2w$:
write_inwf Script asks you for the first and last index of f energies $Nmin, Nmax$ (see above).
Next it requires:

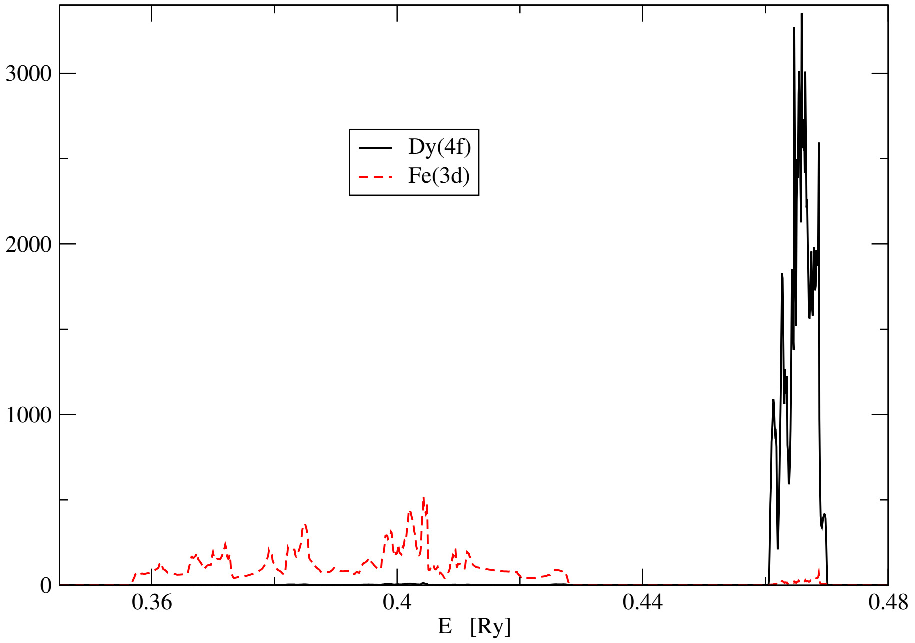

FIG. 4: $Dy_2Fe_2Si_2C$. Density of states projected on Fe(3d) and Dy(4f) states. Δ = -0.3 Ry.

> next proj.
i.e. indexes of atoms and orbital character of wannier functions (wf) to be calculated. E.g. if they are on 5th atom (not kinds of atoms, but all atoms are counted - use *file.struct* to determine the index) enter:
5:f
If there are more atoms with f states proceed analogously to include all these atoms.
Next write input for wannier90:
write_win num_iter 1000
wannier90.x -pp case, preliminary wannier90 calculation.
x w2w (-p) w2w calculation
wannier90.x case wannierization.

After finishing the above sequence, inspect *case.wout*. If the wannier90 converged to correct results, the spread of each f wf should be of order of 1 or smaller, depending on how large is the hybridization. The wf should be located at (or very near to) the R atomic positions. In $DyAlO_3$ and $Dy_2Fe_2Si_2C$ the average spread is ~ 0.3 and 0.4 $\AA^2$, respectively.

IV. FOURTH STEP: CALCULATION OF CRYSTAL FIELD PARAMETERS

The program *bkq*, necessary for this step is in:
CFP_manual/4th_step/programs
The *w2w* and *wannier90* programs can handle also p and d states and this holds also for *bkq*.

wannier90 most important result for CFP calculation is the hamiltonian transformed to Wannier basis. It is saved in file *case_hr.dat*. This file should be copied to *fort.7*.

Program *bkq* is used to determine the crystal field parameters. This program needs two subroutines: *trafo.f*, *transf.f* and the *lapack* library. The compilation is made using the *Makefile*. In addition *bkq* also needs explicit form of spherical tensors. These were extracted from modified output of *lanthanide* package and written on file *Cqk_d* and *Cqk_f* for d and f states ,respectively. These files may be found in
CFP_manual/4th_step
In single run *bkq* calculates CFP of selected atom and selected l. The run can be repeated for other atom and other l, providing that corresponding wf were calculated.

To calculate the CFP for f electrons:

```
cp Cqk_f fort.90
cp case_hr.dat fort.7
bkq<case.inbkq>case.outbkq
cp fort.8 case.cfp
```

The input *case.inbkq*:
line 1
$nat, icfp, lcfp, inhr, iwf, ipr, iprt, iprf, iprcqk$
nat: number of atoms for which Wannier functions were calculated.
$icfp$ index of atom for which CFP will be calculated.
$lcfp$ orbital number for which CFP will be calculated.
$inhr$ =0 for older wannier90 versions (before 2012), =1 for more recent versions.
$inhr$ is required because of different format of *case_hr.dat* in older and newer versions.
iwf =0 ordering of wf in present version of $w2w$
iwf =1 ordering of wf in old version of $w2w$ (prior ~ 2012)
$ipr, iprt, iprf, iprcqk$ printing options for main program, trafo, transf and C_q^k
line 2
$indat(i), nlorb(i), (lorb(i, j), j = 1, nlorb(i))$
$indat(i)$ index of atom
$nlorb(i)$ number of orbital numbers of wf on this atom
$lorb(i, j)$ orbital numbers of wf on this atom
line 2 is repeated nat-times.

Example for DyAlO$_3$ with for Dy atoms/unit cell:
4 1 3 1 0 2 0 0 0
1 1 3
2 1 3
3 1 3
4 1 3

The program first extracts the local $4f$ hamiltonian $\hat{h}_{loc}$ (n x n hermitean matrix, $n = 2*lcfp+1$) from *case_hr.dat* ($fort.7$). Next $\hat{h}_{loc}$ is expanded in a series of spherical tensor operators $\hat{C}_q^{(k)}$:

$$\hat{h}_{loc} = \sum_{k=2,4,6} \sum_{q=-k}^{k} B_q^{(k)} \hat{C}_q^{(k)}. \tag{1}$$

To find $B_q^{(k)}$ we make use of the fact that $\hat{C}_q^{(k)}$ form complete orthogonal set of operators in the subspace of f (or d or p) states. Then

$$B_q^{(k)} = \frac{1}{n_{k,q}} \sum_{i=1}^{n} \sum_{j=i}^{n} h_{loc}^{i,j} C_q^{(k),(i,j)}, \tag{2}$$

where $n_{k,q}$ is the normalizing factor:

$$n_{k,q} = \sum_{i=1}^{n} \sum_{j=i}^{n} C_q^{(k),(i,j)} C_q^{(k),(i,j)}. \tag{3}$$

Using above equations bkq calculates all independent CFP having odd k (three real, twelve complex for f states). Understandably those $B_q^{(k)}$ not allowed by the symmetry are equal to zero. File *case.cfp* ($fort.8$) contains crystal field parameters in cm^{-1} written in the format that is used as the input file for 'REcfp' in the V step.
Important:

- CFP are referred to the coordinate system in which the WIEN2k calculations (steps 1, 2) were performed.
- CFP with odd k are not calculated by bkq. The reason is that matrix elements of corresponding $\hat{C}_q^{(k)}$ in the f (or d) subspace are zero.

V. FIFTH STEP: USING REcfp PROGRAM

Program for this step are in:
CFP/5th_step/programs/SRC_REcfp)

Program 'REcfp' is modified 'lanthanide'[1] and it calculates eigenenergies and eigenvectors of atom (ion) with f^n (also p^n and d^n, which are, however, treated without three body and spin-orbit corrections) electron configuration. The hamiltonian includes:

- free ion terms (e-e repulsion, spin-orbit coupling).
- Zeeman interaction.
- Exchange interaction in molecular field approximation (not yet fully tested).
- Crystal field interaction.

On input it requires

- 19 parameters of free ion hamiltonian.
- Magnitude and direction of external magnetic field and exchange field.
- Crystal field parameters.

While 'lanthanide' is written in C, 'REcfp' is written in fort90, the C part is called as a subroutine.

In most cases we used the parameters of free ion hamiltonian as determined by Carnall et al.[2]. For Nd and Er impurities in $YAlO_3$ we checked that if other sets of parameters are used, the effect on the multiplet splitting and magnetism is only marginal. The parameters of Carnall in format used as input for 'lanthanide' are in
CFP_manual/5th_step/RE_param/RE.inp (RE=Ce, Pr.......Yb).

REcfp execution

```
cp case.cfp fort.8
cp RE.inp fort.7
REcfp<case.inrecfp>case.outrecfp
cp fort.66 case.energy
```

Explanation of *RE.inp*

```
electrons l RANGE STORE    number of electrons  L  0 0
R2 R4 R6 S2 S4 S6          1. 1. 1. 0. 0. 0.
F2 F4 F6 xi                Slater integrals, s-o coupling constant [cm-1]
Alpha Beta Gamma           Trees parameters  [cm-1]
T2,T3,T4,T6,T7,T8          Casimir parameters [cm-1]
M0 M2 M4 P2 P4 P6          Judd parameters [cm-1]
Bx By Bz                   external field [T]
Bex_x Bex_y Bex_z          exchange field [T]
```

For meaning of Trees, Casimir and Judd parameters see[1,2]
Input to *REcfp case.inrecfp*

line 1 nel,l,nstate,nv
line 2 ipr,iprd,iprm,iprb,iprcfp

1st line
nel is number of electrons
l is orbital quantum number
nstate: if 0, all eigenvalues are calculated, else only *nstate* eigenvalues are calculated
nv: if = 1 only energies are printed on fort.66, if nv = 2 also eigenvectors are printed
2nd line
$ipr, iprd, iprm, iprb, iprcfp$ printing options in different parts of program. The bigger ipr, the longer corresponding output.
We put in the subdirectory CFP_manual/5th_step/RE_param/ the inputs *RE.inrecfp* with *nstate* corresponding to the ground (L, S, J) multiplet of RE (with exception of Eu^{3+} for which we put *nstate*=9, which corresponds to three low lying multiplets). If you are interested in higher lying multiplets, increase *nstate*, eventually put *nastate*=0, in which case energy of all states originating from $4f^{nel}$ configuration will be calculated.

For *nv*=1 case.energy consists of *nstate* lines
i ε_i $[cm^{-1}]$ ε_i $[meV]$ $\varepsilon_i - \varepsilon_1$ $[meV]$
i is the index, ε_i the energy of the eigenstate. i=1 corresponds to the ground state.

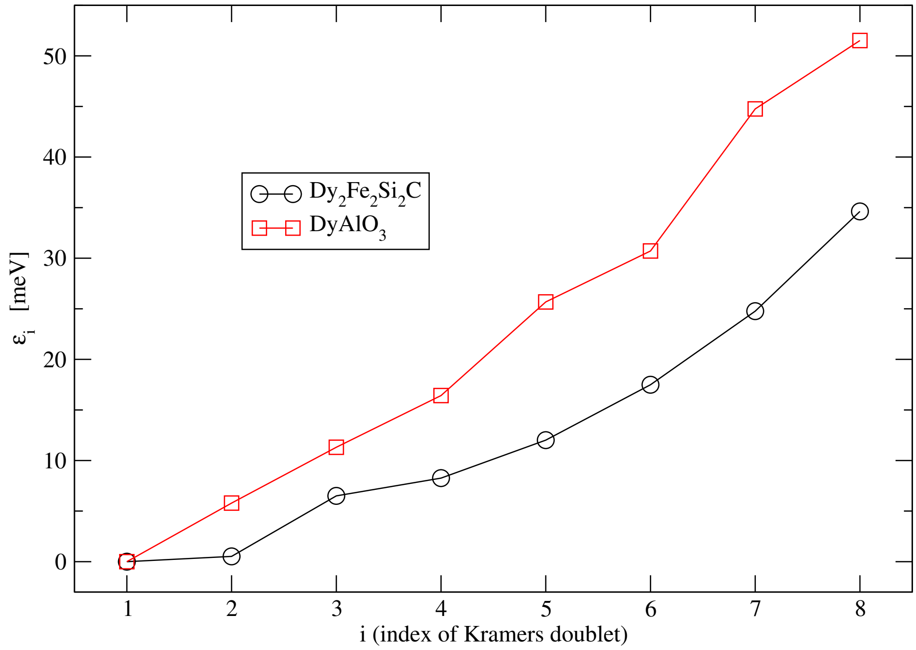

FIG. 5: Splitting of the ground multiplet of the Dy^{3+} ion. Hybridization parameter Δ = -0.3 Ry and -0.6 Ry for Dy$_2$Fe$_2$Si$_2$C and DyAlO$_3$, respectively.

For nv=2 case.energy consists of line with the energy ε_i as described above followed by N_b lines:
$j \quad cr_j \quad ci_j$
N_b is number of basis functions
cr_j and ci_j are real and imaginary parts of the coefficient of jth basis function in the linear combination defining the ith eigenfunction.

Crystal field splitting of the ground multiplet of the Dy^{3+} ion in DyAlO$_3$ and Dy$_2$Fe$_2$Si$_2$C is shown in Fig. 5.

VI. SIXTH STEP: MAGNETIC PROPERTIES

To calculate magnetic properties, several programs in 6th_step/programs are used. Putting magnetic field $\vec{B} \neq 0$ in RE.inp (5th step), dependence of the energy levels ε_i on $\vec{B}$ is determined and, from $\varepsilon_i(\vec{B})$ the magnetic properties are calculated. Original version of the method used $\varepsilon_i(\vec{B})$ to calculate the $\hat{g}$ tensor and van Vleck susceptibility $\hat{\chi}_{vV}$. These programs are still there, though during last two years they were modified. However, in several systems we found out that the eigenenergies intersect as the field is increased. This makes description of magnetism in terms of $\hat{g}$ and $\hat{\chi}_{vV}$ difficult or even impossible. As an alternative, which is safer and can be used in all cases the field dependence of the free energy is calculated and from it the magnetism is determined. This approach is, however, more CPU demanding and not yet fully checked, so if there is no level crossing it is preferable to use programs based on $\hat{g}$ and $\hat{\chi}_{vV}$. The problem of crossing levels can be in some cases circumvented by calculating $\hat{g}$ and $\hat{\chi}_{vV}$ in separate intervals of $|B|$ in which crossing has little effect.

Examples of the crossing levels are displayed in Figs. 6 (Dy$_2$Fe$_2$Si$_2$C) and 7 (DyAlO$_3$).

When comparing theory with the experiment the sum must be made over all R ions in the elementary cell.

Program *changeb* changes the external field on line 7 of the RE.inp$\equiv$ $fort.7$ (5th step).
Input file *case.inchangeb* consists of single line:
$ncomp, (icomp(i), dbcomp(i), i = 1, ncomp)$
where $ncomp$ is number of components to be changed, $icomp(i)$ is index of component (1, 2, 3 correspond to the three orthogonal axes x, y, z) and $dbcomp(i)$ is corresponding increment.

Usually repeated change of the field is required. To change by the same increment the field n-times the following sequence of commands is used:

```
cp RE.inp fort.7
cp case.cfp fort.8
for (( i=1; i <=n; i++ ))
```

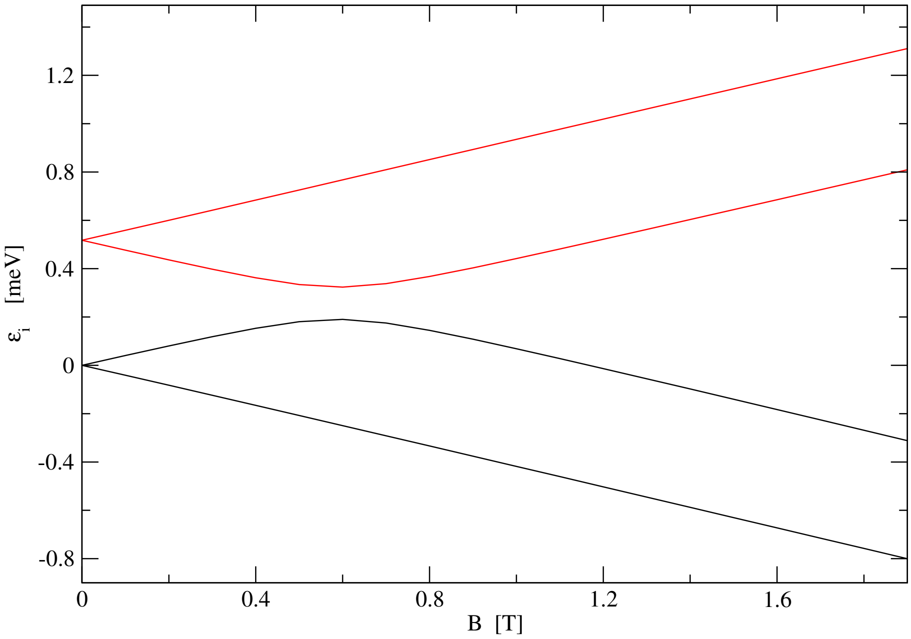

FIG. 6: $Dy_2Fe_2Si_2C$. Dependence of the four lowest eigenenergies on external field $\vec{B}\,||\,a$. Hybridization parameter Δ = -0.3 Ry.

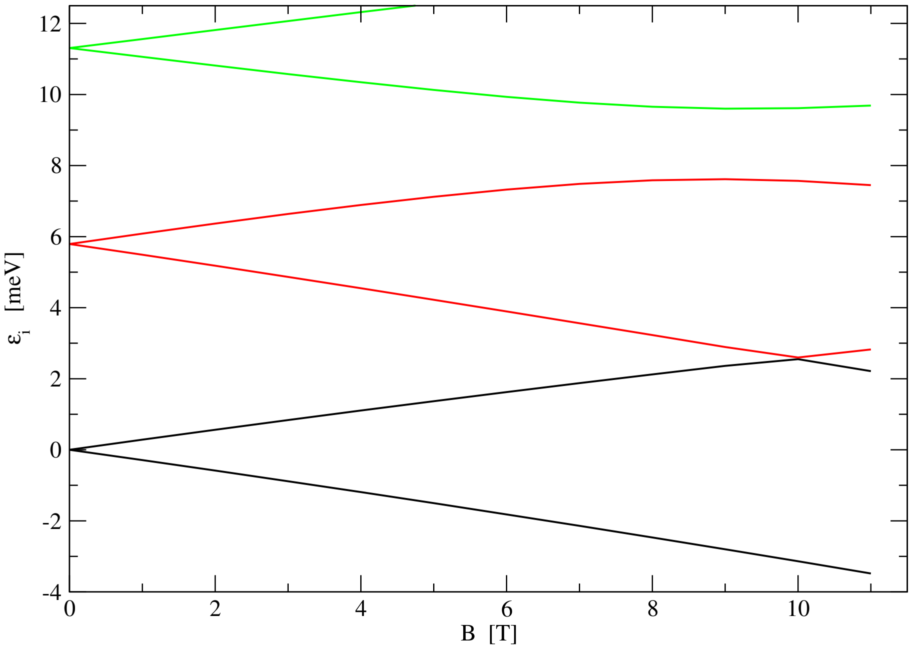

FIG. 7: $DyAlO_3$. Dependence of the low lying eigenenergies on external field $\vec{B}\,||\,a$. Hybridization parameter Δ = -0.6 Ry.

```
do
 CFP_manual/5th_step/programs/REcfp < case.inrecfp >>case.outrecfp
 CFP_manual/6th_step/programs/changeb<case.inchangeb
  cat fort.66 >>case.energy
done
```

In this script n should be even as $n/2$ is number of $\vec{B}$ changes.

Program *changeb_ang* changes the direction of external field (line 7 of *case.inrecfp*). Starting direction is determined automatically from starting values of B_x, B_y, B_z on line 7 of $fort.7$, magnitude of the

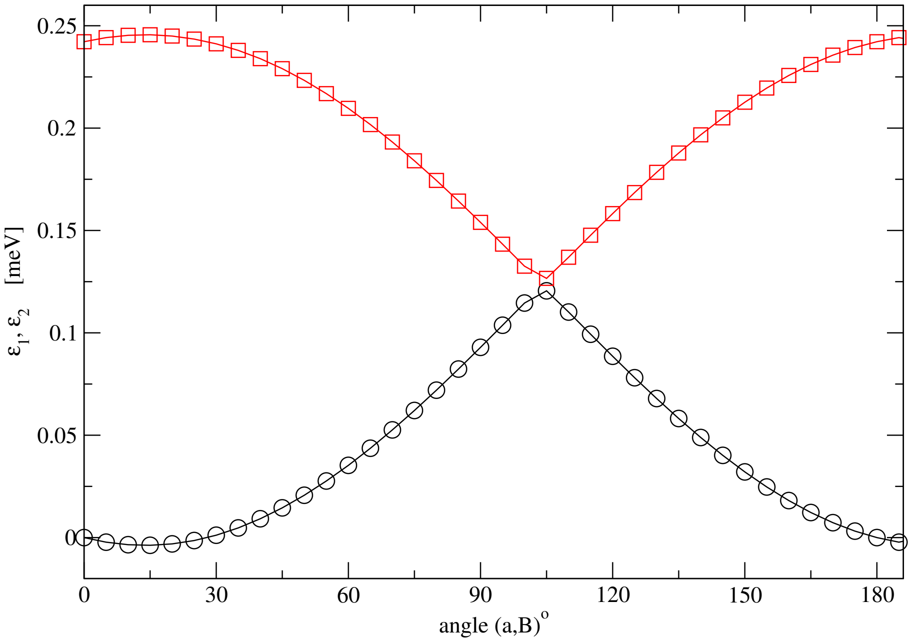

FIG. 8: $Dy_2Fe_2Si_2C$. Dependence of the lowest and first excited eigenenergies on angle which external field $\vec{B}$ makes with axis a. $\vec{B}$ is confined to (ab) plane, $|B|$=0.3 T. Hybridization parameter Δ = -0.3 Ry.

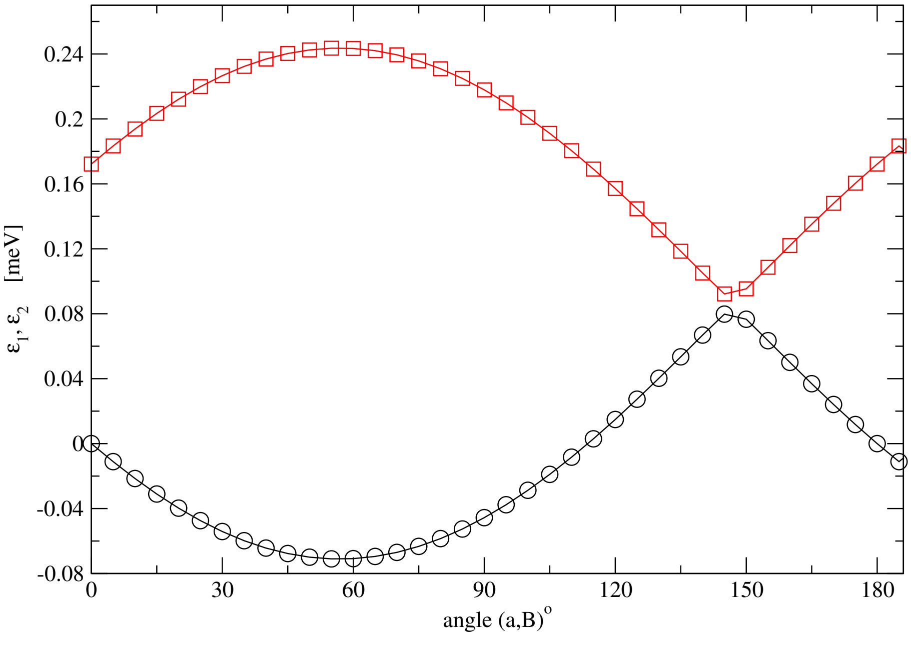

FIG. 9: $DyAlO_3$. Dependence of the lowest and first excited eigenenergies on angle which external field $\vec{B}$ makes with axis a. $\vec{B}$ is confined to (ab) plane, $|B|$=0.3 T. Hybridization parameter Δ = -0.6 Ry.

field must be nonzero.
The input file *case.inchangeb_ang* consists of single line:
nex dth dphi
nex if = 1 external field is changed, if = -1 exchange field is changed
dth, *dph* are increments of azimuthal and polar angles in degrees
The examples are shown in Figs. 8 and 9.
changeb_ang program allows to determine principal axes (x, y, z) for the magnetic moment. In Figs. 8 and 9 x, y are rotated by an angle $\alpha \sim 14^o$ ($Dy_2Fe_2Si_2C$) and 57^o ($DyAlO_3$) from axes a, b, while axis $z \parallel c$.

Program *bhelp* rewrites the *case.energy* to a form more suitable for further processing, as plotting $\varepsilon_i(B)$ dependence, determination of field dependence of free energy or calculation of $\hat{g}$, $\hat{\chi}$ tensors. Parameter nv in *case.inrecfp* of the above script must be equal to 1 in order that *case.energy* contains only energies, not eigenvectors. *bhelp* can also be used to process data calculated by *changeb_ang*.

To execute the program:

```
cp case.energy fort.66
CFP_manual/6th_step/programs/bhelp<case.inbhelp>case.outbhelp
mv fort.9 case.E_B
mv fort.41 case.E_Bplot1.dat
mv fort.42 case.E_Bplot2.dat
```

case.inbhelp consists of single line:
$nb, nstates, nplot, b0, db, ipr$
nb: number of B
$nstates$ number of states calculated for each B
$nplot$ plotting option - see below
$b0$ starting value of B [T]
db increment of B [T]
ipr printing option.

If $nplot = 0$, file $fort.9$ is created. This file consists of $nb * nstates$ lines, each line containing
B [T] ε_i [meV] index(B) i (index of state)
if $nplot$=1, there are also $nfile = nstates/12 + 1$ output files written on fort.41 .... fort.40+nfile. Each of these files contains nb lines and each line consists from up to 13 numbers:
$B \quad \varepsilon_i(B) \quad i = nstart, nend$
$fort.41$ starts with $i = 1$ and ends with $i = \min(12, nstates)$
if $nstates > 12$ then $fort.42$ starts with $i = 13$ and ends with $i = \min(24, nstates)$, etc.

For processing *changeb_ang* results the quantities nb, $b0$, db should be number of angles, starting angle $[^o]$ and angle increment $[^o]$.

A. Programs calculating and using g-factors and vanVleck susceptibility

Program *regr* calculates from $\varepsilon_i(B)$ dependence the components of $\hat{g}$ and $\hat{\chi}_{vV}$ using the quadratic regression. It can be used to analyze data for $\vec{B}$ along one or more (up to four) directions. For $\vec{B}$ along single direction the program is executed by:

```
cp case.E_B fort.27
CFP_manual/6th_step/programs/regr<case.inregr>case.outregr
mv fort.36 case.E0_g_chi
mv fort.9 case.accuracy
```

Input file *case.inregr* consists of single line
$nbe, nstate, ndir, ipr$
nbe number of magnetic fields
$nstate$ number of eigenstates
$ndir$ number of components, $ndir$=1, for calculation along single direction of $\vec{B}$.
To determine magnetism more completely it is necessary to repeat calculation for several directions of $\vec{B}$. An example are orthorhombic perovskites, for which four calculations with $\vec{B} \parallel a$, b, c and [110] are needed[4] to characterize magnetism fully. It is then of advantage to save $\varepsilon_i(B)$ dependencies as well as results of the *bhelp* program in subdirectories a, b, c and 110. The execution of *regr* program is then

```
cp a/case.E_B fort.27
cp b/case.E_B fort.28
cp c/case.E_B fort.29
cp 110/case.E_B fort.30
CFP_manual/6th_step/programs/regr<case.inregr>case.outregr
```

```
mv fort.36 case.E0_g_chi
mv fort.9 case.accuracy
```

File *case.E0_g_chi* consists of
index of state, $\varepsilon_i(B=0)$ [meV], $g_1 \dots g_{ndir}$; g-factor components
index of state, $\varepsilon_i(B=0)$ [meV], $\chi_{vV,1} \dots \chi_{vV,ndir}$; χ_{vV} components $[\mu_B/T]$
these two lines are repeated *nstate*-times.
File *case.accuracy* may be used to check the accuracy of quadratic regression. It consists of $nstate * nbe$ lines
B $\varepsilon_i(B)$ of REcfp $\varepsilon_i(B)$ of regression, $\sum_1^i$ of squares of differences.

Often the canonical components of $\hat{g}$ and $\hat{\chi}_{vV}$ are needed, in particular when calculating magnetism in polycrystals. In the original version of the manual canonical form of $\hat{g}$ and $\hat{\chi}_{vV}$ could be calculated for R-ions in orthorhombic perovskites. This possibility is no longer supported. Instead, the principal directions of the magnetic moment can be determined using the angular dependence of eigenenergies in fixed magnitude of external field as calculated by program *changeb_ang*.

Program *temp* calculates temperature dependence of magnetic moment and susceptibility for fixed external field using the file *case.E0_g_chi* calculated by *regr*. To execute *temp*:

```
cp case.E0_g_chi fort.36
CFP_manual/6th_step/programs/temp<case.intemp>case.outtemp
```

The input *case.intemp* consists of single line
$nstate$, $ndir$, nT, $T0$, dT, B, dB $nstate$, $ndir$ these quantities have the same meaning as in *case.inregr*
nT, $T0$, dT, B, dB
nT is number of temperature steps
$T0$ is the starting temperature in K
dT is increment of temperature in K
B is magnitude of field in T
dB is change of B for calculating the derivative.
For each temperature program determines magnetic moment m for fields $B-dB$, B, $B+dB$ using the Boltzman statistics. Susceptibility is then calculated as numerical derivative

$$\chi = \frac{m(B+dB) - m(B-dB)}{2\,dB}$$

dB must be sufficiently small, for the derivative to be reliable.
Program *highT*
highT may be used providing that the thermal energy kT is much larger than the change of eigenenergies in the magnetic field. The execution, input and output are analogous as in program *temp*.

B. Programs calculating magnetism directly from free energy

These programs require that eigenenergies are calculated for a set of closely spaced fields, so that the 2nd derivative of the free energy F with respect to B is reliable. For each field the magnetic moment is determined as a numerical derivative of F

$$m(T) = -\frac{\partial F}{\partial B};\ F(B) = -kT \ln z(B);\ z(B) = \sum_{i=1}^{N} \exp(-\frac{\varepsilon_i(B)}{kT}).$$

The susceptibility is then calculated as derivative of the magnetic moment:
$\chi = \partial m / \partial B$.

Program *freeEB* calculates dependence of the magnetic moment and susceptibility on external magnetic field B for selected temperature.
To execute the program:
cp case.energy fort.66
CFP_manual/6th_step/programs/$freeEB$ $<$ $case.infreeEB$ $>$ $case.outfreeEB$
cp fort.24 $freeEB.dat$ Input file $case.infreeEB$ consists of single line:

1st line
nstates, T, nB, $B0$, dB, *ipr*
nstates is number of states.
T [K] is temperature for which calculation is made.
nB is number of fields, nB should be ≥ 5.
$B0$ [T] is starting value of the field.
dB [T] is increment of field.
ipr is printing option.
For $ipr = 1$ the output *case.outfreeEB* consists of

```
Field dependence of M and chi from free energy
nstates,nb,T
```

and nB lines containing

```
B[T]        freeE[K]      m[muB]      chi[emu/mol]    1/chi[mol/emu]
```

File *freeEB.dat* contains *nb* last lines of the output. It can be thus directly used to plot the results using e.g. *xmgrace*.

Program *freeET* calculates dependence of the magnetic moment and susceptibility on temperature for single selected magnetic field.
To execute the program:
cp case.energy fort.66
CFP_manual/6th_step/programs/*freeET* < *case.infreeET* > *case.outfreeET*
case.energy should contain eigenenergies for five fields $B - 2dB$, $B - dB$, B, $B + dB$, $B + 2dB$.
To execute *freeET*:
cp case.energy fort.66
CFP_manual/6th_step/programs/*freeET*¡*case.infreeET* > *case.outfreeET*
cp fort.24 *freeET.dat* Input file *case.infreeET* consists of single line:
nstates, B, dB, nT, $T0$, dT, *ipr*
nstates is number of states.
B [T] is field for which calculation is made.
dB [T] is increment of field.
nT is number of temperatures.
$T0$ [K] is starting value of temperature.
dT [K] is increment of temperature.
ipr is printing option.
Output *case.outfreeET* and file *freeET.dat* are analogs of *freeEB* outputs, but with temperature interchanged with the external field.

Comparison of temperature dependence of magnetic moment using programs *freeET*, *temp* and *highT* are shown in Figs. 10 ($Dy_2Fe_2Si_2C$) and 11 (DyAlO3).

C. Averaging in polycrystals

Program *tempav* calculates temperature dependence of susceptibility and magnetic moment in polycrystals, using the canonical form of $\hat{g}$ and $\hat{\chi}_{vV}$ as stored in file *case.E0_g_chi* calculated by program *regr*. It is working for Kramers ions providing that two components of every Kramers doublet follow each other in *case.E0_g_chi*. For non-Kramers ions its use is problematic, particularly if there are pseudodoublets as often happen for Tb^{3+}.
To execute *tempav*:

```
cp case.E0_g_chi fort.36
CFP_manual/6th_step/programs/tempav<case.intempav>case.outtempav
```

File *case.E0_g_chi* should contain three principal values of $\hat{g}$ and $\hat{\chi}_{vV}$.
The input *case.intemptav* consists of three lines:
First line
kramers, *nstate*
kramers=1 for Kramers ions, =0 for non-Kramers ions.
nstate is number of eigenstates
Second line
nphi, *nx*; see below the explanation.
Third line

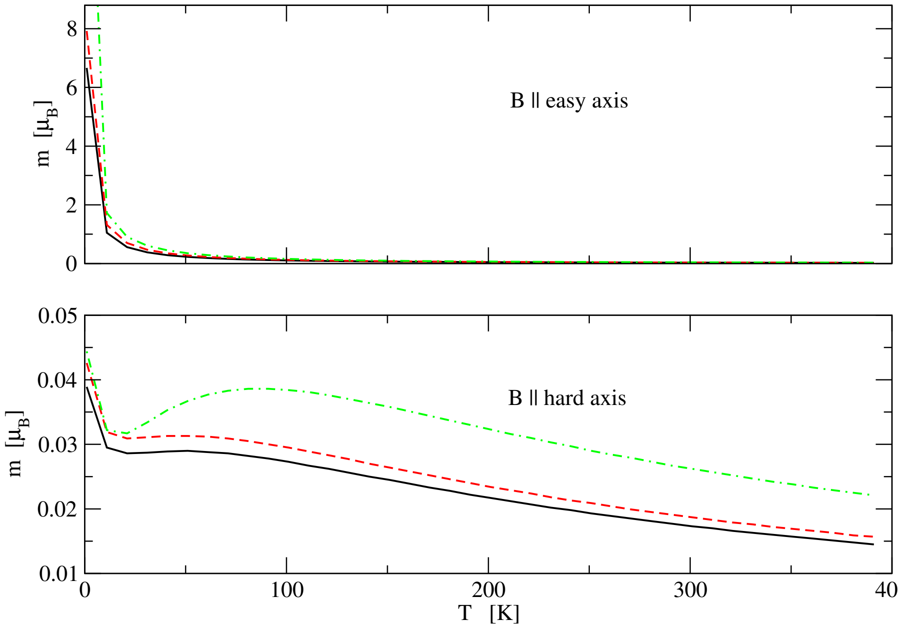

FIG. 10: $Dy_2Fe_2Si_2C$. Temperature dependence of magnetic moment calculated by programs $freeET$ (full curve), *temp* (dashed curve) and $highT$ (dashed-dot curve). $|B|$= 0.3 T, hybridization parameter Δ = -0.3 Ry. Easy and hard axes lie in the (ab) plane, easy axis makes an angle $\sim 14^o$ with axis a.

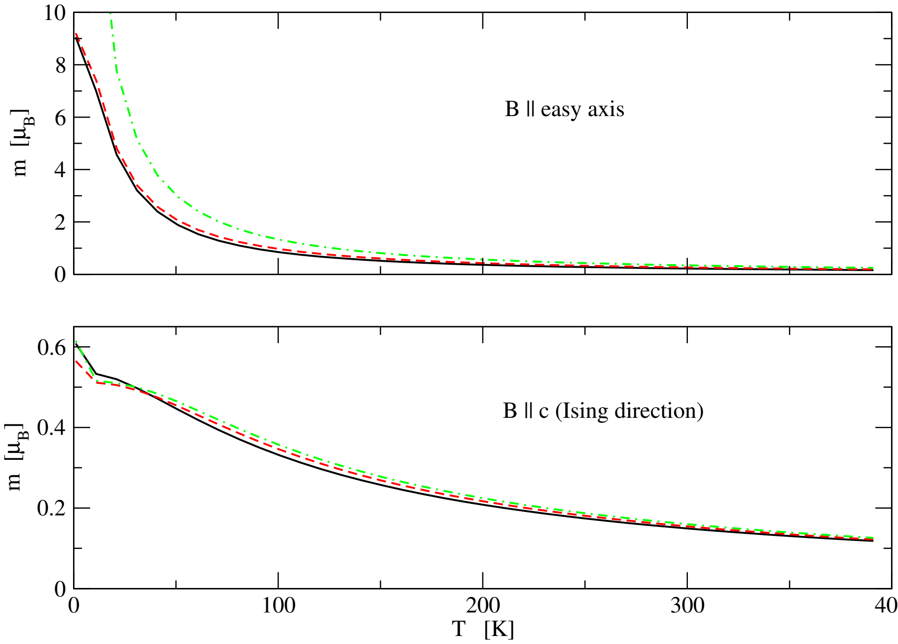

FIG. 11: $DyAlO_3$. Temperature dependence of magnetic moment calculated by programs $freeET$ (full curve), *temp* (dashed curve) and $highT$ (dashed-dot curve). $|B|$= 2 T, hybridization parameter Δ = -0.6 Ry.

$nT, T0, dT, B, dB$ these quantities have the same meaning as in *case.intemp*
Magnetic moment is calculated as in program *temp* for magnetic field parallel to direction characterized by azimuthal and spherical angles ϕ, θ. Denoting $x = \cos(\theta)$ the averaging is performed by numerical integration with $0 \leqq \phi \leqq \pi$, $0 \leqq x \leqq 1$
$nphi$, nx are numbers of (equidistant) angle ϕ and $\cos(\theta)$.

program $highT$ can be used for both Kramers and non-Kramers ions to calculate temperature dependence of the susceptibility. It uses the invariance of

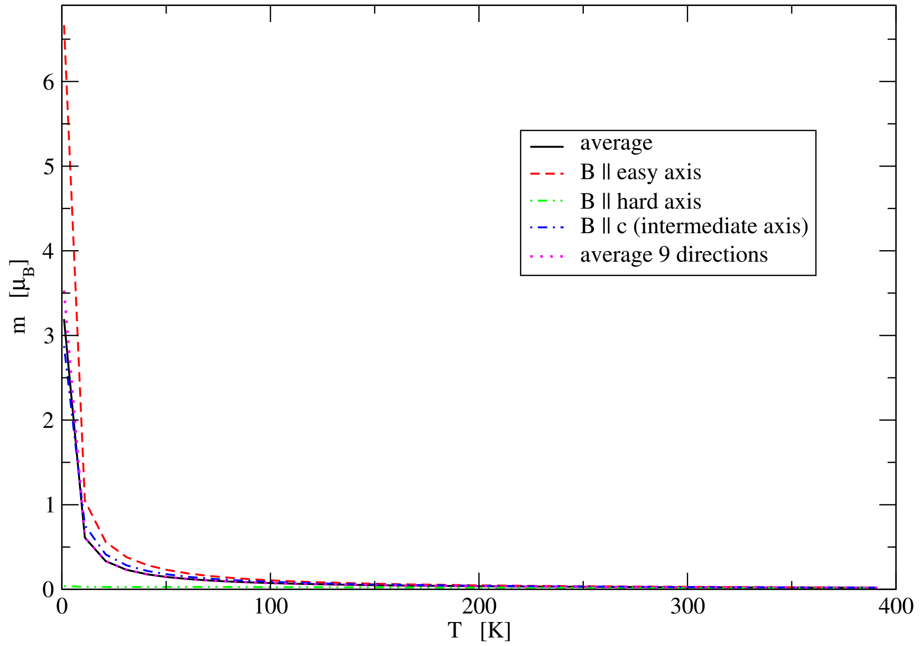

FIG. 12: $Dy_2Fe_2Si_2C$. Temperature dependence of magnetic moment calculated by programs $freeET$ with the field = 0.3 T along principal axes. The simple average is shown by full curve. Hybridization parameter Δ = -0.3 Ry. Easy and hard axes lie in the (ab) plane, easy axis makes an angle $\sim 14^o$ with axis a.The dotted line (average 9 directions) corresponds to the average taken over a, b, c, axes and over directions [110], [$\bar{1}$10], [101], [$\bar{1}$01], [011], [0$\bar{1}$1].

$$g_{xx}^2 + g_{yy}^2 + g_{zz}^2, \; \chi_{xx}^2 + \chi_{yy}^2 + \chi_{zz}^2$$

The file *case.E0_g_chi* thus must contain $\hat{g}$ and $\hat{\chi}_{vV}$ components calculated for $\vec{B}$ parallel to three orthogonal directions. Program then automatically calculates the average, which is printed in the output.

Programs $freeEB$, $freeET$ can be used without limitation on relative magnitude of thermal and magnetic energy for both Kramers and non-Kramers ions. However, their application may require a lot of CPU because of the necessity to integrate numerically when the averaging is performed. In a simplified approach the results for polycrystals may be approximated by taking the average of results calculated for $\vec{B}$ along the principal directions of magnetic moment (eventually adding further directions to the averaging process). Results of this procedure are shown in Figs. 12 ($Dy_2Fe_2Si_2C$) and 13 (DyAlO3). Fig. 12 indicates that for $Dy_2Fe_2Si_2C$ the simplification is satisfactory. For the averaging can be used program

program $aver$.

To execute $aver$:

```
cp  dir1/freeET.dat fort.21
cp  dir2/freeET.dat fort.22
.
.
.
cp  dirndir/freeET.dat fort.20+ndir
CFP_manual/6th_step/programs/aver<case.inaver>case.outaver
```

Input *case.inaver* consists of two lines

First line

$ndir$, nt, where $ndir$, nt are number of directions and temperatures, respectively,

Second line

$(w(idir), idir = 1, ndir)$, where $w(idir)$ is the weight (= multiplicity) of the direction $idir$.

To understand this manual our papers[3–7] and the user-guides to WIEN2k, wien2wannier and wannier90 should be

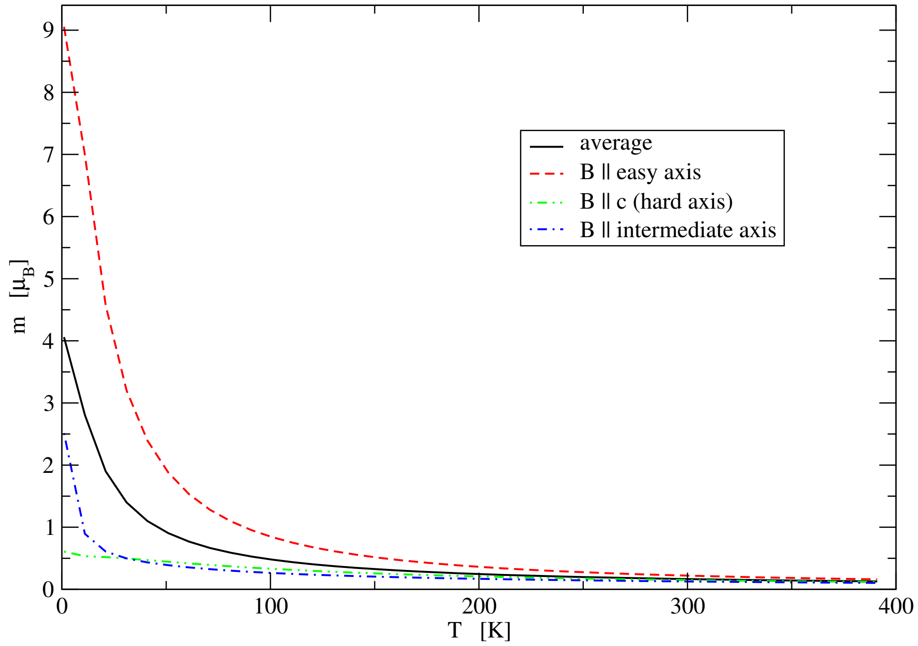

FIG. 13: DyAlO$_3$. Temperature dependence of magnetic moment calculated by program *freeET* with the field = 2 T along principal axes. The simple average is shown by full curve. Hybridization parameter Δ = -0.6 Ry. Easy and intermediate axes lie in the (ab) plane, easy axis makes an angle $\sim 57^o$ with axis a.

consulted.

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