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Thermal, single-ionic magnetic properties of materials calculated with Atomic Matters MFA computation system

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Atomic Matters MFA is a computation system for predicting properties of defined materials in a magnetic ordered state and around phase transition temperature. The scientific methodology and software structure makes it an intuitive application for performing magnetocaloric effect (MCE) research. The application calculation algorithm is based on an atomic, localized-electron approach and Mean Field Approximation (MFA) methodology.

Atomic Matters MFA provides magnetic, calorimetric and electronic properties of atomic-like localized electron systems under the influence of:

- **Crystal Electric Field (CEF)**,
- **Spin-Orbit coupling (LS coupling)**,
- **Magnetic interactions (Zeeman Effect)**, taken as both Mean Field Approximation (MFA) and the influence of external, user-defined magnetic fields.

The application combines quantum electronic properties of correlated electron systems with calculations for properties of bulk crystals of a defined material. The application has an intuitive, interactive graphic interface with many unique tools for easy, fast and fruitful work. The 3D Visualization of CEF potentials, easy import and export of data and rapid calculation results gives users a unique chance to form an opinion on the effect of defined interactions, simplifications, calculation spaces etc. for the macroscopic properties of crystals of a defined material.

Atomic Matters MFA is an extension of the **Atomic Matters** application, a system for describing the Fine Electronic Structure according to **CEF, Spin-Orbit and Zeeman interactions** and predicting basic magnetic, electronic and spectral properties of materials in a **stable paramagnetic state**.

Atomic Matters computation system key features:

- Intuitive Graphic User Interface with interactive 3D visualizations of CEF
- Units and Convention Calculators and Point Charge Model Toolset
- Energy Level Scheme Viewer and Absorption Spectra Simulator
- Internal Database of $<r^n>$ and Easy Import & Export of Data
- Informative Thermal Diagrams of: Magnetic Susceptibility $\chi(T)$, $\chi(T)^{-1}$, Specific Heat c(T), Entropy S(T) and more...

Atomic Matters MFA provides macroscopic properties of materials in defined temperature regions, especially in **ordered state** and around phase transition temperature, such as:

- Magnetic Moment in Ordered State: **m**(T) (spin, orbit, directional components)
- Thermal Evolution of Energy Level positions, Eigenstates: $E^i(T)$, $\Gamma^i(T)$,
- Free Energy vs. Temperature in a definable temperature region: F(T),
- Localized Electron Specific Heat: $c_{el}(T)$ (and Debye, crystal lattice contribution),
- Magnetocrystalline Anisotropy constants: $K_1(T)$, $K_2(T)$, $K'_2(T)$, $K_3(T)$, $K_4(T)$,
- Localized Electron Entropy: S(T) with a useful toolset for curve comparison and $-\Delta S(T)$ calculations for **Magnetocaloric Effect (MCE)** research.

The magnetic face transition can be simulated by **Atomic Matters MFA** according to Mean Field Approximation methodology. The calculations are realized using only one user-defined 'free parameter' n_{mol} which defines molecular magnetic field strength $\mathbf{B}_{mol}$ according to the simple relation of ion magnetic moment **m** at the current temperature:

$$\mathbf{B}_{mol}(T) = n_{mol}\,\mathbf{m}(T)$$

The value of parameter n_{mol} defines phase transition temperature T_c for self-consistent magnetic interactions in defined ionic/atomic system.

THEORETICAL APPLICATION BACKGROUND

Atomic Matters Hamiltonian: — **Calculation space:**

$$H_{J\,CEF} = \sum_n \sum_m B_n^m \hat{\mathbf{O}}_n^m(J, J_z) + g_L\,\mu_B\,\mathbf{J}\cdot\mathbf{B}_{ext} \qquad |J, J_z>$$

$$H_{LS\,CEF} = \sum_n \sum_m B_n^m \hat{\mathbf{O}}_n^m(L, L_z) + \lambda\mathbf{L}\cdot\mathbf{S} + \mu_B(\mathbf{L} + g_e\mathbf{S})\cdot\mathbf{B}_{ext} \qquad |L,S,L_z\,S_z>$$

Atomic Matters MFA Hamiltonian:

$$H_{J\,mol} = \sum_n \sum_m B_n^m \hat{\mathbf{O}}_n^m(J, J_z) + n_{mol}\,g_L^2\,\mu_B^2\left(-\mathbf{J}<\mathbf{J}> + \frac{1}{2}<\mathbf{J}>^2\right) + g_L\,\mu_B\,\mathbf{J}\cdot\mathbf{B}_{ext} \qquad |J, J_z>$$

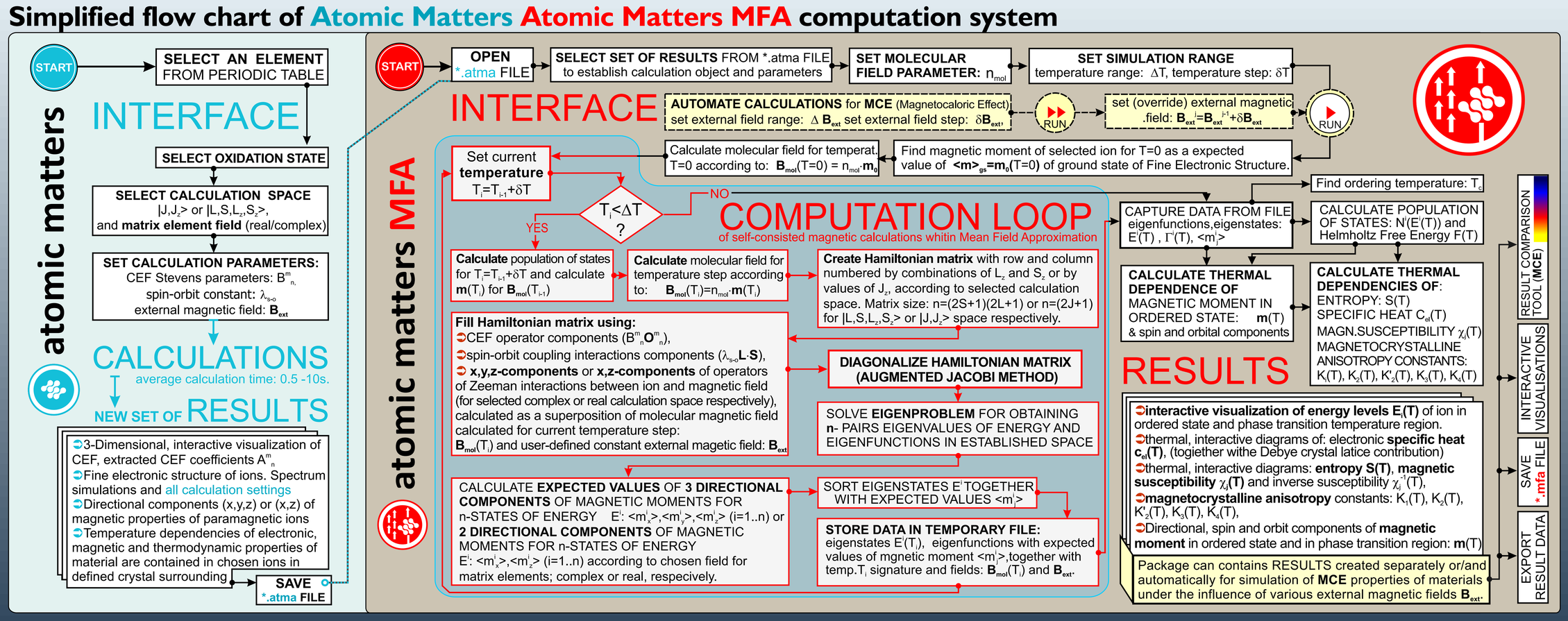
$$H_{LS\,mol} = \sum_n \sum_m B_n^m \hat{\mathbf{O}}_n^m(L, L_z) + \lambda\mathbf{L}\cdot\mathbf{S} + n_{mol}\,\mu_B^2\left(-(\mathbf{L}+g_e\mathbf{S})<\mathbf{L}+g_e\mathbf{S}> + \frac{1}{2}<\mathbf{L}+g_e\mathbf{S}>^2\right) + \mu_B(\mathbf{L}+g_e\mathbf{S})\cdot\mathbf{B}_{ext} \qquad |L,S,L_z\,S_z>$$

THERMODYNAMICS & MACROSCOPIC PROPERTIES

- statistical Sum of States: $Z(T) = \mathrm{Tr}\left(\exp\left(-\frac{\hat{\mathbf{H}}}{k_B T}\right)\right) = \sum_i \exp\left(-\frac{E_i(T)}{k_B T}\right)$
- Helmoltz Free Energy: $F(T) = -k_B T \ln Z(T)$
- localized electron specific heat: $c_{mol}(T) = -T\left(\frac{\partial^2 F(T)}{\partial T^2}\right)$
- entropy of localized electron system: $S(T) = S(0) + \int_0^T \frac{c(T)}{T}\,dT$
- magnetic moment in ordered state: $m_J^\alpha(T) = \frac{g_L\mu_B}{Z(T)} \sum_i <J_\alpha^i> \exp\left(-\frac{E_i(T)}{k_B T}\right)$

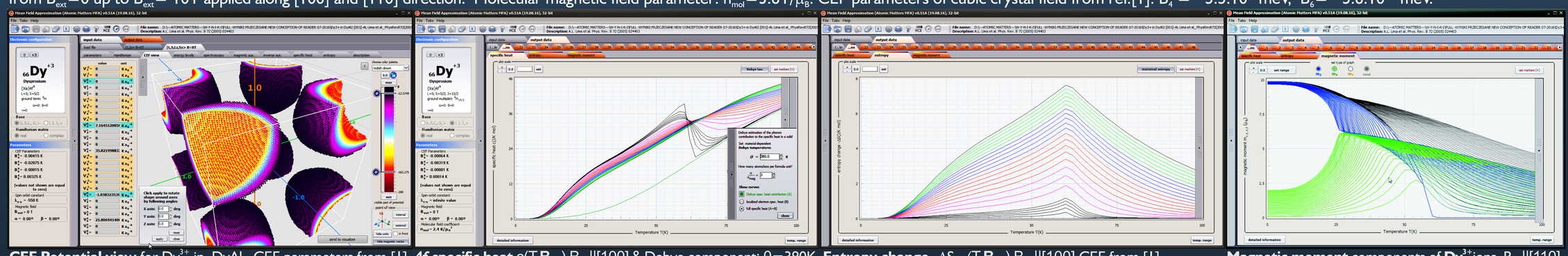
$$m_{LS}^\alpha(T) = \frac{\mu_B}{Z(T)} \sum_i <L_\alpha^i + g_e S_\alpha^i> \exp\left(-\frac{E_i(T)}{k_B T}\right)$$

Simplified flow chart of Atomic Matters Atomic Matters MFA computation system

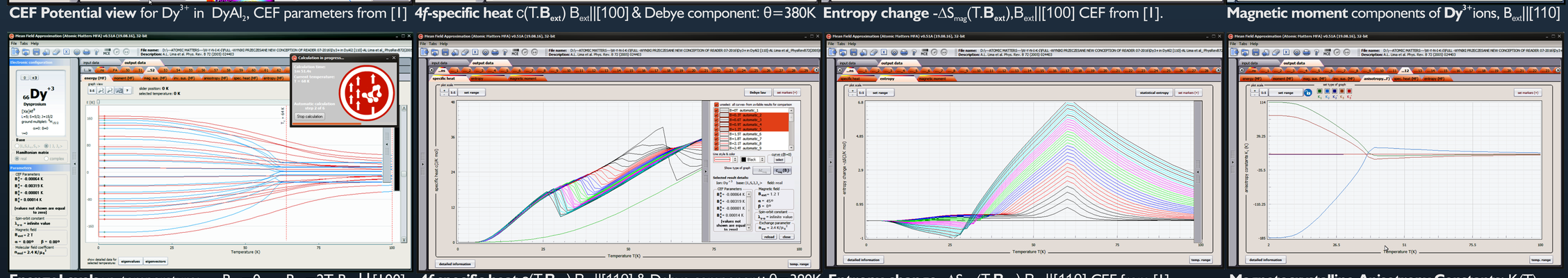


Atomic Matters MFA calculation results. Example of: Dy^{3+} ions in $DyAl_2$

Screenshots of **Atomic Matters MFA** application captured during calculations Dy^{3+}ions in $DyAl_2$ crystal lattice in various external magnetic field from $B_{ext}=0$ up to $B_{ext}=10$T applied along [100] and [110] direction. Molecular magnetic field parameter: $n_{mol}=3.6T/\mu_B$. CEF parameters of cubic crystal field from ref.[1]: $B_4=-5.5.10^{-5}$meV, $B_6=-5.6.10^{-7}$ meV.



CEF Potential view for Dy^{3+} in $DyAl_2$, CEF parameters from [1] **4*f*-specific heat** $c(T.\mathbf{B}_{ext})$ $B_{ext}||[100]$ & Debye component: $\theta=380K$ **Entropy change** $-\Delta S_{mag}(T.\mathbf{B}_{ext}),B_{ext}||[100]$ CEF from [1]. **Magnetic moment** components of Dy^{3+}ions, $B_{ext}||[110]$



Energy Levels vs. temperature: — $B_{ext}=0$, — $B_{ext}=2T$, $B_{ext}||[100]$, **4*f*-specific heat** $c(T.\mathbf{B}_{ext})$ $B_{ext}||[110]$ & Debye component: $\theta=380K$ **Entropy change** $-\Delta S_{mag}(T.\mathbf{B}_{ext}),B_{ext}||[110]$ CEF from [1]. **Magnetocrystalline Anisotropy Constants:** $K_i(T)$.

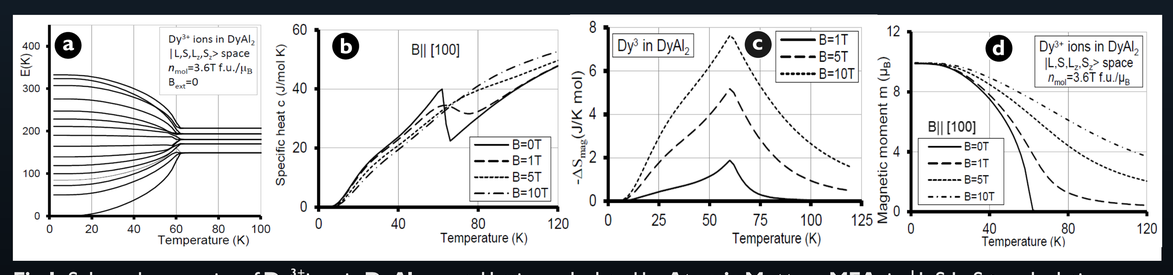


Fig 1. Selected properties of Dy^{3+}ions in $DyAl_2$ crystal lattice, calculated by **Atomic Matters MFA** in $|L,S,L_z,S_z>$ calculation space with molecular magnetic field parameter: $n_{mol}=3.6T/\mu_B$. CEF parameters of cubic Crystal Field: $B_4=-5.5.10^{-5}$meV, $B_6=-5.6.10^{-7}$ meV taken from ref [1]: a) Ground part of Electronic Level Structure vs. temperature, calculated for Dy^{3+} ions in $DyAl_2$, $\mathbf{B}_{ext}=0$. b) 4*f*-electron components of molar specific heat with Debye crystal lattice component ($\theta=380$K) vs. temperature under the influence of an external magnetic fields $\mathbf{B}_{ext}$ parallel to [100]. c) Magnetic entropy change $-\Delta S_{mag}(T.\mathbf{B}_{ext})$, for an external magnetic field $\mathbf{B}_{ext}$ parallel to [100]. d) Magnetic moment of Dy^{3+} ions in $DyAl_2$, under the influence of an external magnetic field $\mathbf{B}_{ext}$ =0, 5T and 10T, respectively. The results are in excellent agreement with relevant experimental measurements from ref.[2].

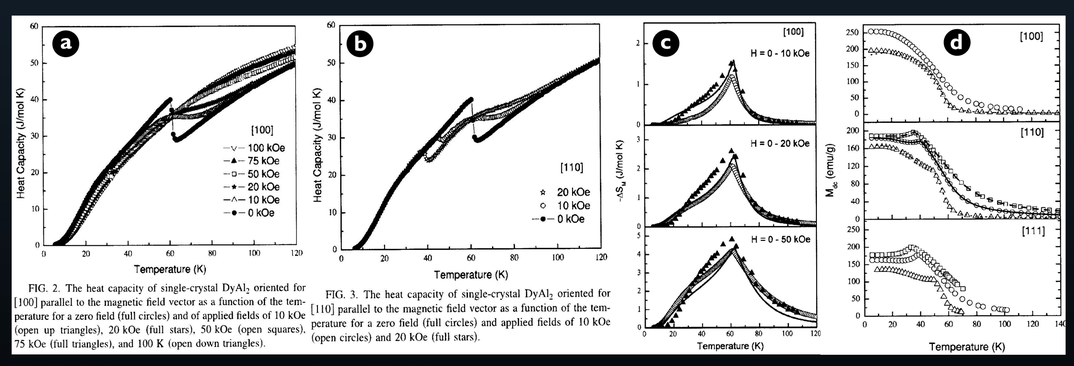


FIG. 2. The heat capacity of single-crystal $DyAl_2$ oriented for [100] parallel to the magnetic field vector as a function of the temperature for a zero field (full circles) and of applied fields of 10 kOe (open up triangles), 20 kOe (full stars), 50 kOe (open squares), 75 kOe (full triangles), and 100 K (open down triangles).

FIG. 3. The heat capacity of single-crystal $DyAl_2$ oriented for [110] parallel to the magnetic field vector as a function of the temperature for a zero field (full circles) and applied fields of 10 kOe (open circles) and 20 kOe (full stars).

Fig 2. Reference experimental data of $\mathbf{DyAl_2}$ single crystal captured from ref.[2]: a) heat capacity measured for B_{ext} along [100], b) heat capacity for B_{ext} along [110]. c) entropy change for B_{ext} along [100], d) DC magnetization.

REFERENCES

[1] H.G. Purwins, A. Leson, *Adv. Phys.* **39** (1990) 309,
[2] A.L. Lima et al. *Phys. Rev.* **B** 72 (2005) 024403.

We kindly invite your cooperation in testing and developing **Atomic Matters Atomic Matters MFA** software. Do not hesitate to contact us: **r.michalski@induforce.eu**