Thermomagnetic properties of $DyAl_2$ single crystal, calculated by ATOMIC MATTERS MFA Computation System

RAFAŁ MICHALSKI, JAKUB ZYGADŁO
INDUFORCE
M.Pszona 41/29 31-462 Cracow
POLAND
JAGIELLONIAN UNIVERSITY,
Faculty of Mathematics and Computer Science,
Łojasiewicza 6 30-348 Cracow,
POLAND
r.michalski@induforce.eu   http://www.atomicmatters.eu

Abstract: We present the results of calculations of properties of $DyAl_2$ single crystals performed with our new computation system called ATOMIC MATTERS MFA [1,2]. A localized electron approach methodology was applied to describe the electronic structure evolution of Dy ions over a wide temperature range and estimate Magnetocaloric Effect (MCE). Thermomagnetic properties of $DyAl_2$ were calculated based on the fine electronic structure of the $4f^{n9}$ configuration of the Dy atom. Our calculations yielded: magnetic moment value and direction; single-crystalline magnetization curves in zero field and in external magnetic field applied in various directions $\mathbf{m}(T,\mathbf{B}_{ext})$; the 4*f*-electronic components of specific heat $c_{4f}(T,\mathbf{B}_{ext})$; and temperature dependence of the magnetic entropy and isothermal entropy change with external magnetic field $-\Delta S(T,\mathbf{B}_{ext})$. The cubic universal CEF parameters values used for all CEF calculations was taken from [3] and recalculated for universal cubic parameters set for the RAl_2 series A_4=+7.164Ka_0 and A_6 =-1.038Ka_0. Magnetic properties were found to be anisotropic due to cubic Laves phase C15 crystal symmetry. These studies reveal the importance of multipolar charge interactions when describing thermomagnetic properties of real 4f electronic systems and the effectiveness of an applied self-consistent molecular field in calculations for magnetic phase transition simulation.

Key-Words: - $DyAl_2$, $ReAl_2$, Laves Phase, CEF, MFA, MCE, Atomic Matters.

1 Introduction

Condensed matter science research in advanced magnetic refrigerant materials has focused on the giant magnetocaloric effect since its discovery. This has advanced the development of near room-temperature magnetic cooling technology.

The RAl_2 (R=rare earth element) compounds are well known intermetallic materials with interesting magnetic properties at low temperatures. The magnetic properties of this series were studied intensively in the 1970s, but a new wave of interest in this compound family has appeared due to research into materials with a large Magnetocaloric Effect (MCE) for future magnetic refrigerators. We present the results of simulations performed by our ATOMIC MATTERS computation system [1,2] of thermomagnetic properties of $DyAl_2$. A few calculation results for the $DyAl_2$ compound are compared with experimental data taken from the literature [3-8]. All the lanthanides combine with aluminum to form an RAl_2 compound with the same crystalline structure. This structure is the so-called cubic Laves phase C15 and the point symmetry for the rare earth ion is $4\bar{3}m$.

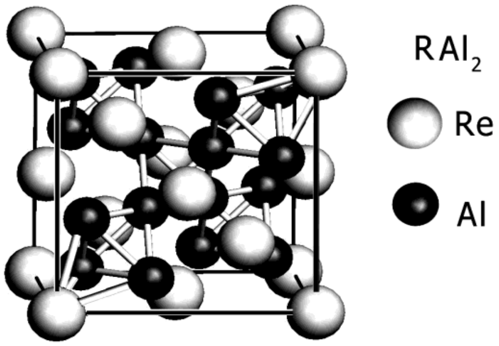

Fig. 1. Cubic elementary cell of RAl_2 Laves phase C15 crystals.

The structure was named after the Swiss crystallographer who performed work on the prototype compound $MgCu_2$. The CEF parameters describing the multipolar charge interaction of R ions in the crystal surrounding in this structure were agreed for both compounds and established by a previous study [3,4,9] for A_4=+7.164Ka_0 and A_6 =-1.038Ka_0.

2 Computation system

All $DyAl_2$ calculations were performed with ATOMIC MATTERS MFA computation system [2], an extension of the ATOMIC MATTERS application [1] that describes fine electronic structure and predicts basic magnetic and spectral properties of materials in a paramagnetic state. ATOMIC MATTERS MFA calculates magnetic, calorimetric and spectroscopic properties of atomic-like localized electron systems under the influence of Crystal Electric Field (CEF), spin-orbit coupling, and magnetic interactions, taken both as Mean Field Approximation (MFA) self-consistent, dynamic calculations and the influence of established external magnetic fields $\mathbf{B}_{ext}$ [2]. ATOMIC MATTERS MFA calculates macroscopic properties of materials in defined temperature regions, especially around phase transition temperature, such as: magnetic moment $\mathbf{m}(T,\mathbf{B}_{ext})$ (spin and orbital, directional components); localized electron specific heat $c_{4f}(T,\mathbf{B}_{ext})$; localized electron entropy with a useful tool set for MCE; isothermal entropy change $-\Delta S(T,\mathbf{B}_{ext})$ calculations; evolution of energy level positions; total free energy.

Both calculation systems contain advanced Graphic User Interface (GUI) with system of hierarchical tabs for calculation results management, 3D interactive visualizations of potentials and fields based on Open GL graphic engine, tools and databases for convenient and effective work. More in-date information about Atomic Matters computation systems are available on our web page [10].

3 Theoretical background

The theoretical approach applied at the heart of ATOMIC MATTERS MFA computation system is deeply rooted in atomic physics. Taking into consideration the individual population of states of fine electronic structure of ions/atoms at different temperatures according to L. Boltzmann statistics make it possible to define the temperature dependencies of single ionic properties. ATOMIC MATTERS MFA can simulate phase transitions of ionic/atomic systems according to dynamic calculations of the molecular field B_{mol}, simply defined as:

$$\mathbf{B}_{mol}(T) = n_{mol}\,\mathbf{m}(T) \qquad (1)$$

This interacts with ions to induce their magnetic moments. Such self-consistent calculations can only be performed after establishing the molecular field factor n_{mol} that is closely related to the temperature of phase transitions T_C.

For rapid calculations in a thermodynamically stable temperature region, ATOMIC MATTERS offers the following CEF+Spin-Orbit+Zeeman Hamiltonian according to the chosen calculation space of ground multiplet |J,Jz> or ground atomic term $|LSL_zS_z>$ respectively[1]:

$$H_J = H_{CEF} + H_{Zeeman} = \sum_n \sum_m B_n^m \hat{\mathbf{O}}_n^m(J,J_z) + g_L \mu_B \mathbf{J}\cdot\mathbf{B}_{ext} \qquad (2)$$

or

$$H_{LS} = H_{CEF} + H_{S\text{-}O} + H_{Zeeman} =$$

$$= \sum_n \sum_m B_n^m \hat{\mathbf{O}}_n^m(L,L_z) + \lambda \mathbf{L}\cdot\mathbf{S} + \mu_B(\mathbf{L} + g_e \mathbf{S})\cdot\mathbf{B}_{ext} \qquad (3)$$

For all Hamiltonians: $B^m{}_n$ denotes CEF parameters, $\mathbf{O}^m{}_n$ are Stevens operators, λ-is the spin–orbit constant, and g_L and $g_e \approx$ 2.002319 are the gyromagnetic factors of a whole ion or single electron respectively. For a whole ion or electron respectively, μ_B is the Bohr magneton and $\mathbf{B}_{ext}$ is the external magnetic field. In all cases, calculations in the $|LSL_zS_z>$ space are more physically appropriate due to their completeness, but traditional calculations with base $|JJ_z>$ can be also performed by our computation systems for comparisons and rapid estimations [2]. For calculating properties in temperatures around the magnetic phase transition point, a self-consistent methodology for molecular field calculation called Mean Field Approximations (MFA) is applied. The idea behind this method is the estimation of direction and value of the magnetic field (molecular field) generated by ions at a defined temperature, and calculation of the influence of this magnetic field for electronic state structures of ions. In a selected calculation space, according to eq.1 we define a molecular field as an expected value of the total moment of the 4f electronic subshell multiplied by the molecular field, inter ionic exchange factor n_{mol}:

$$\mathbf{B}_{mol} = -n_{mol}\, g_L \mu_B < \mathbf{J} > \qquad (4)$$

or

$$\mathbf{B}_{mol} = -n_{mol}\, \mu_B < \mathbf{L} + g_e \mathbf{S} > \qquad (5)$$

Where g_L and $g_e \approx$ 2.002319 are the gyromagnetic factors. On the basis of the calculated electronic level structure $E_i(T)$, the directional components of magnetic moments are established for all identical ions. This means that Hamiltonian matrix diagonalization is performed for all defined temperature steps recurrently, in contrast to simple ATOMIC MATTERS calculations [1], which diagonalize matrices one time for a single run and deduce all thermodynamic properties from the stable discrete energy level structure obtained. This self-consistent procedure provides temperature-dependent energy level structure and has one only free parameter, n_{mol}, called the molecular field parameter. The value of n_{mol} is closely related to the phase transition temperature T_C of the macroscopic structure of ions. The formal expression of the full Hamiltonian used by ATOMIC MATTERS MFA computation system, according to the chosen calculation space $|JJ_z>$ or $|LSL_zS_z>$ respectively, has the form:

$$H_{J\,\mathrm{mol}} = H_J + H_{\mathrm{mol}} = +\sum_n \sum_m B_n^m \hat{\mathbf{O}}_n^m (J, J_z) + \\ + n_{\mathrm{mol}}\, g_L^2\, \mu_B^2 \left(-\mathbf{J} < \mathbf{J} > + \frac{1}{2} < \mathbf{J} >^2 \right) + g_L\, \mu_B\, \mathbf{J} \cdot \mathbf{B}_{\mathrm{ext}} \quad (6)$$

or

$$H_{LS\,\mathrm{mol}} = \sum_n \sum_m B_n^m \hat{\mathbf{O}}_n^m (L, L_z) + \lambda \mathbf{L} \cdot \mathbf{S} + \\ + n_{\mathrm{mol}}\, \mu_B^2 \left(-(\mathbf{L} + g_e \mathbf{S}) < \mathbf{L} + g_e \mathbf{S} > + \frac{1}{2} < \mathbf{L} + g_e \mathbf{S} >^2 \right) + \\ + \mu_B (\mathbf{L} + g_e \mathbf{S}) \cdot \mathbf{B}_{\mathrm{ext}} \quad (7)$$

The eigenvectors of the Hamiltonian are described according to the selected calculation base by the total momentum quantum numbers $|JJ_z>$ or spin and orbit quantum numbers $|LSL_zS_z>$. Using the commutation relations of the angular momentum operators, we obtain information about expected values of the projections of magnetic momentum of all electronic states at a chosen temperature [2]:

$$m_J^{\alpha}(T) = \frac{g_L \mu_B}{Z(T)} \sum_i < J_{\alpha}^i > \exp\left(-\frac{E_i(T)}{k_B T} \right) \quad (8)$$

$$m_{LS}^{\alpha}(T) = \frac{\mu_B}{Z(T)} \sum_i < L_{\alpha}^i + g_e S_{\alpha}^i > \exp\left(-\frac{E_i(T)}{k_B T} \right) \quad (9)$$

Where: α indexes directional components, i numbers the Hamiltonian eigenstates, while Γ_i represents the expected value of the total angular momentum along the α-axis in the i-th state:

$$<J^i_{\alpha}> = <\Gamma_i(T)|\, \mathbf{J}_{\alpha}\, |\, \Gamma_i(T)> \quad (10)$$

$$<L^i_{\alpha} + g_e S^i_{\alpha}> = <\Gamma_i(T)|\, \mathbf{L}^i_{\alpha} + g_e \mathbf{S}^i_{\alpha}\, |\, \Gamma_i(T)> \quad (11)$$

All property calculations can be done for 3D (x,y,z) real space by using complex Hamiltonian matrix elements defined by full expressions of extended Stevens $\mathbf{O}^m_n$ operators[11]. Mostly for comparison with traditional calculation results, ATOMIC MATTERS also offers a 2D (x,z) calculation methodology of a simplified model of CEF interactions defined by Stevens $\mathbf{O}^m_n$ operators with real number matrix elements only [12].

Taking into consideration the possibility of the thermal population of states, we automatically obtain the thermal evolution of single ion properties of the whole compound [13,14].

Under the thermodynamic principle at temperature T=0K only the ground state is occupied. In this situation, the magnetic moment of the ion is exactly equal to the momentum of the ground state. If the temperature rises, the probability of occupying higher states increases according to Boltzmann statistics. The number of ions with energy E_i within a system at temperature T is:

$$N_i(T) = N_0 \frac{\exp\left(-\frac{E_i(T)}{k_B T} \right)}{Z(T)} \quad (12)$$

where $N_0 \approx 6.022.1023\ \mathrm{mol}^{-1}$ (Avogadro constant) and $Z(T)$ is the sum of states. Knowing the sum of the states, we can determine the Helmholtz free energy $F(T)$:

$$F(T) = -k_B T \ln Z(T) \quad (13)$$

According to thermodynamic principles, the contribution of localized electrons to the total specific heat of materials can be calculated by numerical derivation of Helmholtz free energy:

$$c_{\mathrm{mol}}(T) = -T \left(\frac{\partial^2 F(T)}{\partial T^2} \right) \quad (14)$$

This makes it possible to calculate entropy according to the well-known definition:

$$S(T) = S(0) + \int_0^T \frac{c(T)}{T} dT \quad (15)$$

The value of electronic entropy for a defined temperature is difficult to compare, but the isothermal change of the entropy of the system at a given temperature is a very important material parameter that describes its thermomagnetic properties. Isothermal Entropy change $-\Delta S(T, B_{\mathrm{ext}})$, captured for different temperatures under the influence of different magnetic fields, is one the most important properties of a material that describes its usefulness as a magnetocaloric material. The value $-\Delta S(T, B_{\mathrm{ext}})$, which was extracted from experimental specific heat measurements, is often presented as a basic description of the Magnetocaloric Effect (MCE) of a material [3-7]. In our approach, isothermal entropy change can be directly calculated from eq.15 according to the definition:

$$\Delta S(T, \mathbf{B}_{\mathrm{ext}}), = S(T, \mathbf{B}_{\mathrm{ext}}=0) - S(T, \mathbf{B}_{\mathrm{ext}}). \quad (16)$$

ATOMIC MATTERS MFA also provides single-ionic magnetocrystalline anisotropy calculations that include full calculations (without Brillouin function approximation) of $K_i(T)$ magnetocrystalline constants for defined temperature ranges according to the relations [15]:

$$K_1(T)=\frac{3}{2}B_2^0\left(\left\langle\hat{\mathbf{O}}_2^0\right\rangle-\left\langle\hat{\mathbf{O}}_2^2\right\rangle\right)-5B_4^0\left(\left\langle\hat{\mathbf{O}}_4^0\right\rangle-3\left\langle\hat{\mathbf{O}}_4^2\right\rangle\right)-$$
$$-\frac{21}{2}B_6^0\left(\left\langle\hat{\mathbf{O}}_6^0\right\rangle-5\left\langle\hat{\mathbf{O}}_6^2\right\rangle\right),$$
$$K_2(T)=\frac{35}{8}B_4^0\left(\left\langle\hat{\mathbf{O}}_4^0\right\rangle-4\left\langle\hat{\mathbf{O}}_4^2\right\rangle+\left\langle\hat{\mathbf{O}}_4^4\right\rangle\right)+$$
$$+\frac{63}{8}B_6^0\left(\left\langle\hat{\mathbf{O}}_6^0\right\rangle-20\left\langle\hat{\mathbf{O}}_6^2\right\rangle+5\left\langle\hat{\mathbf{O}}_6^4\right\rangle\right),$$
$$K_2^*(T)=\frac{1}{8}\left(B_4^0\left\langle\hat{\mathbf{O}}_4^0\right\rangle+5B_6^4\left\langle\hat{\mathbf{O}}_6^4\right\rangle\right),$$
$$K_3(T)=-\frac{231}{16}B_6^0\left\langle\hat{\mathbf{O}}_6^0\right\rangle,\ K_3^*(T)=-\frac{11}{16}B_6^4\left\langle\hat{\mathbf{O}}_6^4\right\rangle. \qquad (17)$$

Where: $\left\langle\hat{\mathbf{O}}_n^m\right\rangle$

denotes thermal expected values of Stevens operators we defined according to C. Rudowicz [11]. The exchange interactions simulated according to MFA methodology defined by eq. 1 provide simulated properties strongly dependent on only one parameter, n_{mol}, which is closely related to the temperature of phase transitions T_C. It is easy to find the value of n_{mol} for correct T_C, but the value of this parameter can be estimated according to De Gennes scaling [16]:

$$T_C \sim G(f^n),\ G(f^n)=(g_L-1)^2J(J+1) \qquad (18)$$

De Gennes scaling is also a useful tool for n_{mol} estimation, as charge surroundings can be transferred between ions in series. The CEF part of Hamiltonian contains Stevens CEF parameters B^m_n. The values of these parameters are only appropriate for the defined ion. The recalculation of B^m_n parameters defined for an ion A in the crystal lattice surrounding of ion B in the same crystalline position follows the simple scheme:

$$B^m_n\ (\text{ion A}) \rightarrow A^m_n \rightarrow B^m_n\ (\text{ion B}) \qquad (19)$$

Stevens B^m_n parameters can be expressed by universal A^m_n parameters, according to the calculation space used, as follows:

$$|J,J_z\rangle;\ B^m_n(J,J_z)=\theta_n(J)\ \langle r_{4f}{}^n\rangle\ A^m_n$$
$$|L,S,S_z,L_z\rangle;\ B^m_n(L,L_z)=\theta_n(L)\ \langle r_{4f}{}^n\rangle\ A^m_n \qquad (20)$$

Where values of 2,4,6 –th power of average radius of 4f shell $\langle r^n\rangle$ have been calculated by many authors using Hartree-Fock-type methodology, and the results can be easily found in the literature. The θ_n parameters are the J or L dependent Clebsh-Gordan- type factors, sometimes called $\alpha.\beta,\gamma$ Stevens factors $\theta_2=\alpha$, $\theta_4=\beta$, $\theta_6=\gamma$, which can be expressed by finite equations available in [17,18]. The values of $\langle r_{4f}{}^n\rangle$ are stored in the system's open database together with a reference. In all calculations, we used the $\langle r_{4f}{}^n\rangle$ values tabulated in [14]. The ability to recalculate CEF parameters between ions and calculation spaces offers a unique chance to establish an acceptable simplification of methodology. The recalculation of CEF parameters in Atomic Matters systems is fully automated, but an explicit Stevens Factors Calculator is also available.

4 Calculation results

The CEF parameters used for $DyAl_2$ were originally estimated by H.G. Purwins and Leson [4] and cited by A. L. Lima et al. [3]. The parameters were provided in cubic Stevens notation: $B_4=-(5.5\pm1.2)\cdot10^{-5}$meV and $B_6=-(5.6\pm0.8)\cdot10^{-7}$ meV. We recalculated the values of Stevens parameters to obtain universal, ion-independent CEF notation A^m_n according to eq.19 and eq.20. The parameters A_4=+7.164Ka$_0$ and A_6 =-1.038Ka$_0$ obtained in this manner define charge surroundings of R ion in a crystal lattice of RAl_2. A visualization of this potential is shown in fig. 2. The triangular shapes that are connected to the location of the coordinating Al ions are located symmetrically in cubic surroundings and reflect the atom position in the elementary cell of Laves phase shown in fig.1.

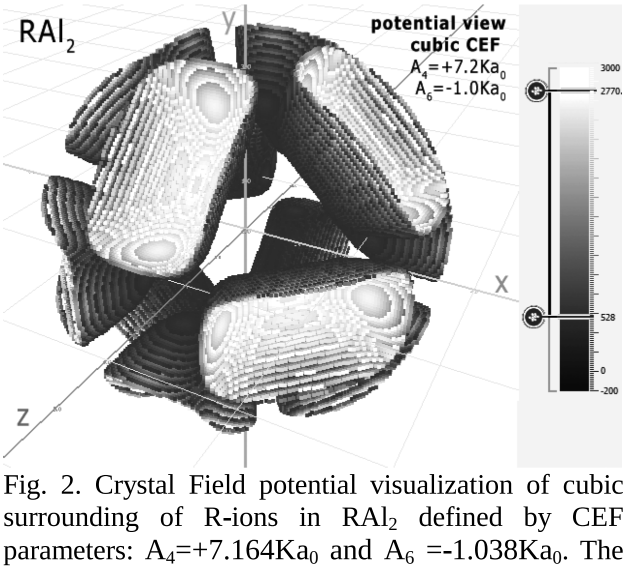

Fig. 2. Crystal Field potential visualization of cubic surrounding of R-ions in RAl_2 defined by CEF parameters: A_4=+7.164Ka$_0$ and A_6 =-1.038Ka$_0$. The visualization of positive sign potential is cut off by the sphere.

The intermetallic compound $DyAl_2$ has strong magnetocaloric properties at low temperatures. This compound has been extensively studied both theoretically and experimentally [3-6].

In this section, we present the results of an investigation of the magnetic and magnetocaloric properties of a DyAl$_2$ single crystal. We have attributed the magnetism of DyAl$_2$ to the Dy ions and calculated the fine electronic structure of the $4f^9$ electronic system in cubic symmetry taking into account the crystal field and inter-site, spin-dependent exchange interactions. The energy level scheme derived is associated with the reduction of the degeneracy of the lowest atomic term ^{6}H given by Hund's first two rules.

The full calculated energy level structure in the |L,S,Lz,Sz> calculation space is shown in fig 3. The obtained overall splitting is strongly dependent on the strength of spin-orbit intra-atomic interactions. We use the free-ion value of spin orbit constant of Ho^{3+} ions λ=-550K and obtain an overall splitting of ^{6}H atomic term of about 15000K = 1.3 eV. Details of ground states structure are shown in fig.4.

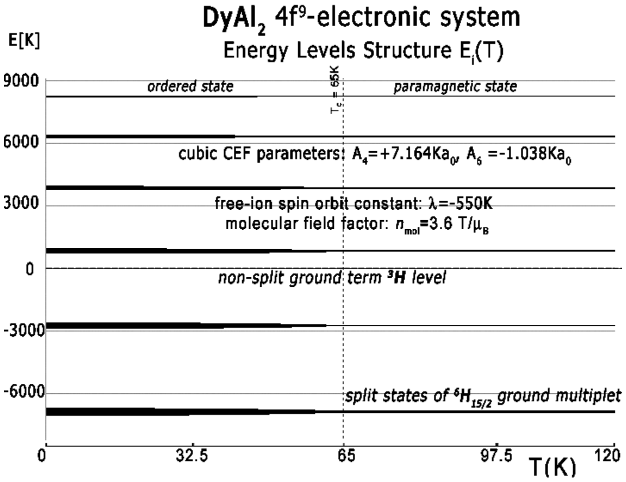

Fig. 3. The result of calculation of energy level position vs. temperature of the fine electronic structure of 4d^9 electronic configuration of Dy ions in DyAl$_2$ in |L,S,Lz,Sz> space under the influence of intra-atomic spin-orbit coupling, inter-atomic self-consistent molecular magnetic field and Crystal Electric Field (CEF).

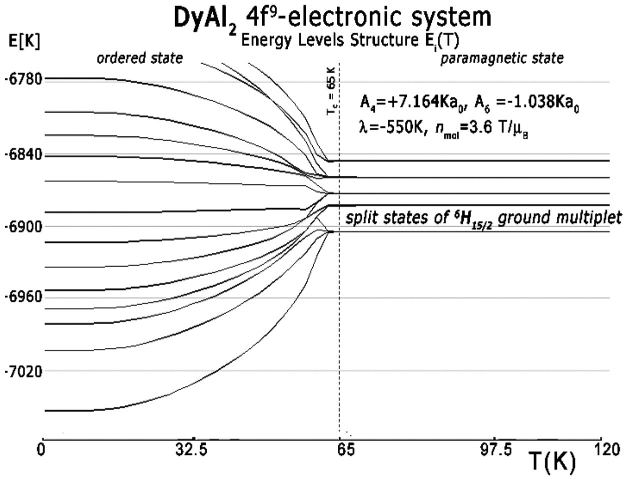

Fig. 4. Ground multiplet energy level structure vs. temperature calculated for 4f^9 electronic system of Dy ions in DyAl$_2$. At Curie temperature T$_C$ =65K, the structure splits under the influence of molecular field and CEF.

In the absence of an external magnetic field, the induced molecular field splits and moves into degenerated states. The value of the molecular field factor established for DyAl$_2$, which reproduces T$_C$ well at about 63K, is n_{mol}=3.6T/μ_B. Above T$_C$, material is in a paramagnetic state and the ground state of Dy ions is degenerated. The ground quartet consists of two quasi doublets. The wave functions of the ground paramagnetic state of Dy ions in DyAl$_2$ can be expressed in |Jz> notation:

Γ_1=-0.137|-5.5>+0.619|-1.5>+0.723|2.5>-0.275|6.5>
Γ_1'=-0.137|5.5>+0.619|1.5>+0.723|-2.5>-0.275|-6.5>
Γ_2=+0.730|-7.5>-0.612|-3.5>-0.303|0.5> -0.026|4.5>
Γ_2'=+0.730|7.5>-0.612|3.5>-0.303|-0.5>-0.026|-4.5>

The molecular field splits these states at T<T$_C$. The value of the molecular field changes and at T=0 (absolute zero) B$_{mol}$=23.6T and its direction is along crystal direction [100], which is the x-axis in our CEF potential picture from fig.2. In this condition, the wave function of the ground singlet gets the form:

Γ_0=0.988|-7.5>-0.153|-3.5>-0.011|0.5>-0.0001|4.5>

The influence of the external magnetic field applied along different crystal directions for the structure of the lowest electronic states is shown in fig.5 and fig.6. The comparison between the effects of the external magnetic field applied along different directions reveals the appearance of an anomaly in the level structure if an external field is applied along crystal direction [110]. This anomaly corresponds to the specific heat curve from fig.7, computed in the same external field direction. The specific heat of $DyAl_2$ (spec. heat of $4f^9$ electronic system +Debye crystal lattice component) shown in fig.7 was calculated for the same external field conditions as experimental measurements from ref.[3]. Excellent agreement between calculated specific heat and experimental data is also confirmed if the external magnetic field is applied along direction [100]. The results of this calculation and reference measurements from ref.[3] are shown in fig. 8.

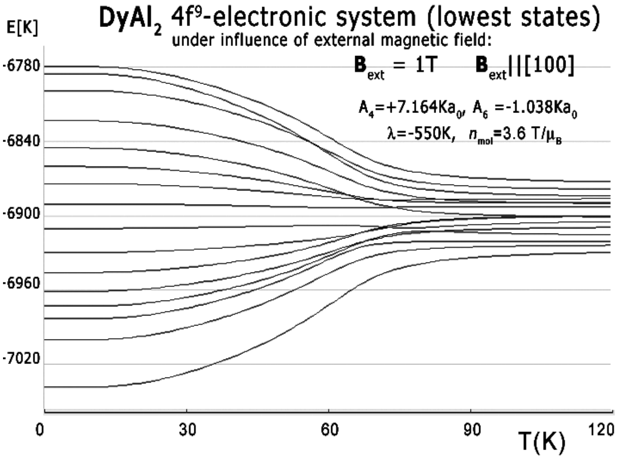

Fig. 5. Ground energy level structure vs. temperature calculated for $4f^9$ electronic system of Dy ions in $DyAl_2$ under influence external magnetic field B_{ext}=1T applied along direction [100]. Parameters of CEF used in calculations and molecular field factor are shown.

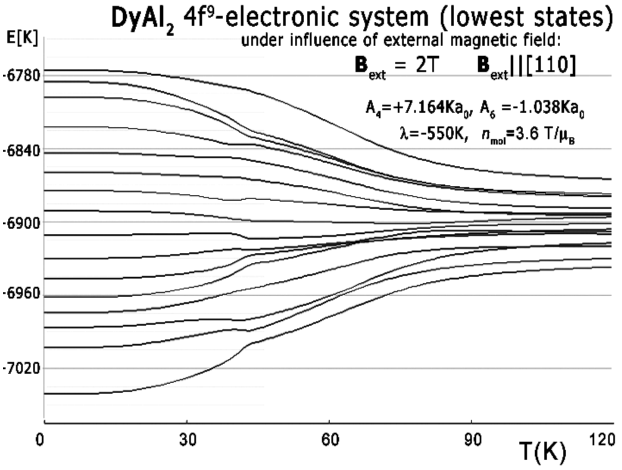

Fig. 6. Ground energy level structure vs. temperature calculated for $4f^9$ electronic system of Dy ions in $DyAl_2$ under influence of external magnetic field B_{ext}=2T applied along direction [110]. Parameters of CEF used in calculations and molecular field factor are shown.

Calculations of electronic structure under the influence of an external magnetic field applied along direction [111] were also performed. Energy level structure calculated for external magnetic field in this direction does not contain anomalies and is similar to calculations performed for $\mathbf{B}_{ext}$ along the easy magnetization direction [100], as shown in fig. 5. Specific heat calculated in these conditions is shown in fig. 8.

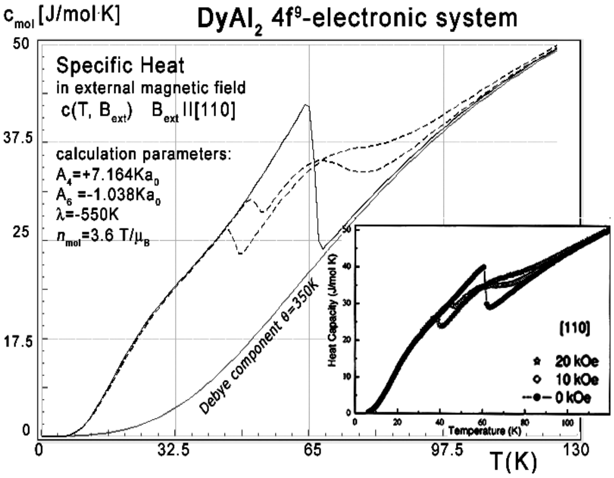

Fig. 7. Calculated $4f$-electron component of molar specific heat (eq.14) with Debye crystal lattice component (θ=350K) vs. temperature for Dy ions in $DyAl_2$, under the influence of an external magnetic field applied along direction [110]. For comparison, the inset shows experimental data from [3] captured in the same external magnetic field conditions as simulated.

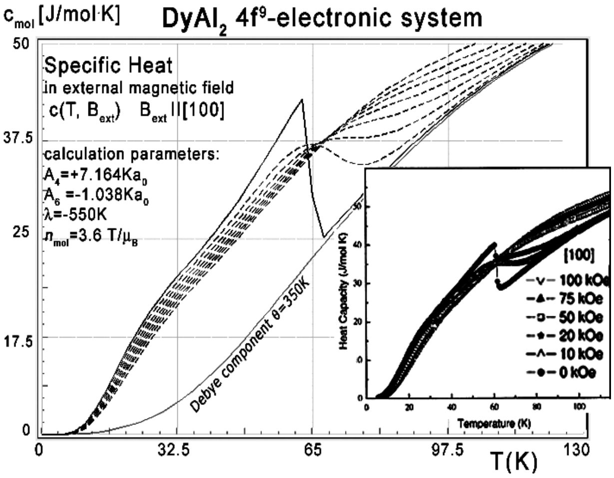

Fig. 8. Calculated $4f$-electron component of molar specific heat (eq.14) with Debye crystal lattice component (θ=350K) vs. temperature of Dy ions in $DyAl_2$, under the influence of an external magnetic field applied along direction [100]. For comparison, the inset shows experimental data from [3] captured in the same external magnetic field conditions as simulated.

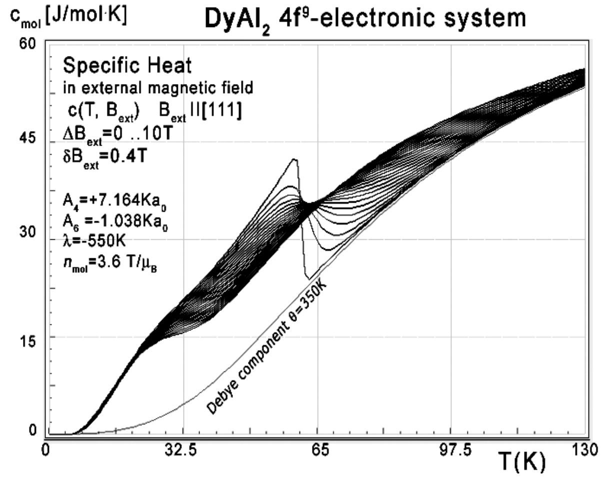

Fig.8. Calculated 4*f*-electron component of molar specific heat (eq.14) with Debye crystal lattice component (θ=350K) vs. temperature of Dy ions in DyAl$_2$, under the influence of an external magnetic field $\mathbf{B}_{ext}$ from 0 to 10T applied along direction [111] .

Collected data of specific heat makes it possible to calculate isothermal entropy change $-\Delta S(T, B_{ext})$ according to eq.16, the same methodology as used by experimentalist [3-7]. Isothermal entropy change calculated with various external magnetic fields applied along all main directions of cubic structure is presented in figs. 9, 10 and 11. The reference data taken from experimental measurement [3] is shown in the insets.

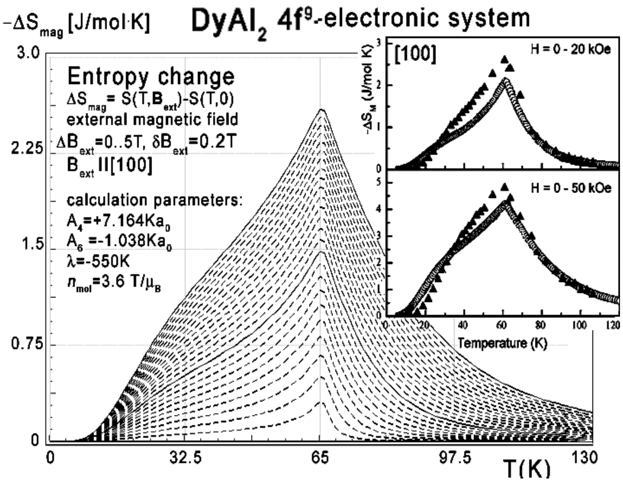

Fig.9. Calculated isothermal entropy change of 4*f*-electronic system vs. temperature (eq.16) of Dy ions in DyAl$_2$, under the influence of various values of external magnetic field from 0 to 5T, with step 0.2T applied along direction [100]. Inset: isothermal entropy change obtained from experimental data; black triangles -extracted from the magnetization, circles - extracted from specific heat, for the DyAl$_2$ single crystal aligned along the same direction, taken from [3]. The solid lines are congruent with the experimental data calculated for the B_{ext}=2T and B_{ext}=5T.

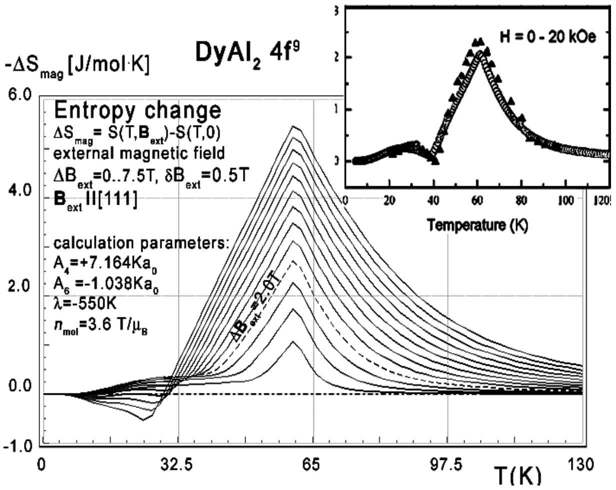

Fig. 10. Calculated isothermal entropy change vs. temperature (eq.16) for various values of external magnetic fields from 0 to 2T with step 0.1T, applied along direction [110] of DyAl$_2$ crystal lattice. Inset: black triangles show isothermal entropy change obtained from experimental data extracted from the magnetization; empty circles show specific heat for a DyAl$_2$ single crystal aligned along the same direction, taken from [3].

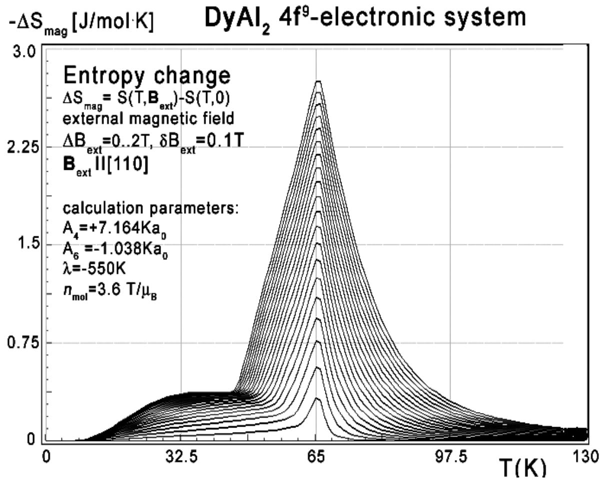

Fig.11. Calculated isothermal entropy change of DyAl$_2$ vs. temperature (eq.16) for various values of external magnetic field from 0 to 2T with step 0.1T, applied along diagonal direction [110].

The anisotropic behavior of calculated thermomagnetic properties is reflected in the magnetocrystalline anisotropy constant calculations.

The results of $K_i(T)$ calculations according to eq.17 in the absence of external magnetic field are shown in fig. 12.

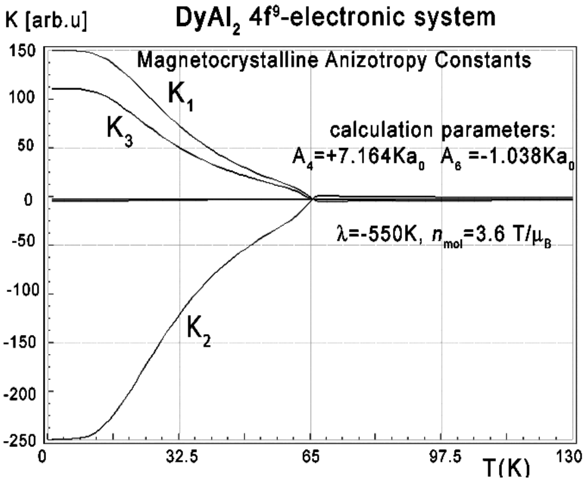

Fig. 12. Calculated according to eq.17, magnetocrystalline anisotropy constants K_1,K_2 and K_3 vs. temperature, calculated for Dy ions in $DyAl_2$ under the influence of CEF and molecular magnetic field.

For completeness, magnetic moment calculations vs. temperature under various external magnetic field conditions were performed. The results of $\mathbf{m}(T,\mathbf{B}_{ext})$ are presented in fig.13, fig.14, fig.15. Fig. 13 clearly confirms direction [100] as an easy magnetization axis. The applied external magnetic field along this direction confirms perfect parallel directions of magnetic vector and external magnetic field (note: in cubic symmetry [100]=[010]=[001]).

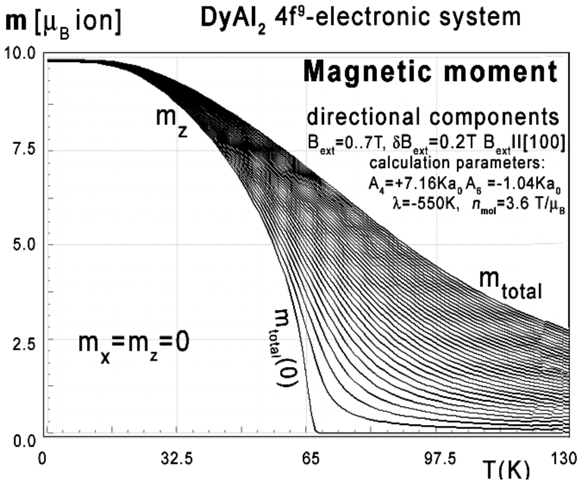

Fig. 13. Calculated x,y,z-directional components of total magnetic moment vs. temperature, calculated for Dy ions in $DyAl_2$ under influence of CEF and molecular magnetic field and various values of external magnetic field from 0 to 7T with step 0.2T applied along direction [100].

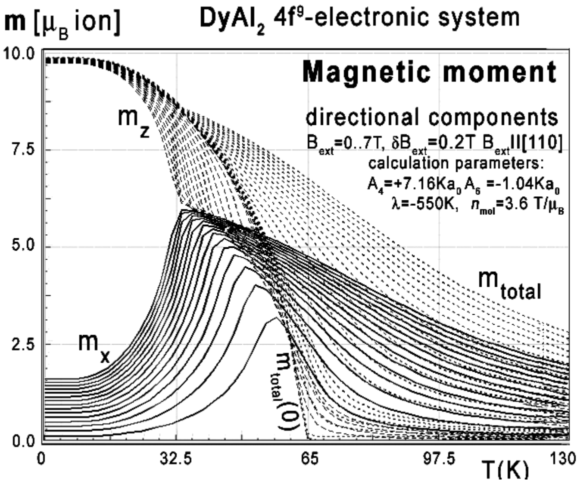

Fig. 14. Calculated x components (solid lines), z-components (dashed lines) of total magnetic moment m_{total} (doted lines) vs. temperature, calculated for Dy ions in $DyAl_2$ under influence of CEF, molecular magnetic field, and various values of external magnetic field from 0 to 7T with step 0.2T applied along direction [110].

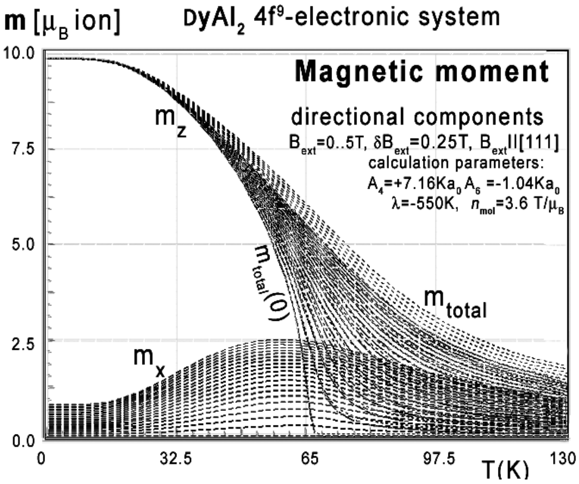

Fig.15. Calculated x components (solid lines), z-components (dashed lines) of total magnetic moment m_{total} (doted lines) vs. temperature, calculated for Dy ions in $DyAl_2$ under influence of CEF, molecular magnetic field, and various values of external magnetic field from 0 to 7T with step 0.2T applied along direction [111].

Magnetic moment calculated in an external magnetic field parallel to direction [110] reveals unusual behavior of the directional component of the total moment. Similar behavior of magnetic moment directions was reported in ref. [3-5]

5 Conclusions

We performed calculations for $DyAl_2$ thermomagnetic properties with the ATOMIC MATTERS MFA computation system. The local symmetry of the Dy ions is cubic, which significantly simplifies the analyses. All the calculations were performed with 2 only cubic CEF parameters and molecular field factor n_{mol}. The excellent agreement obtained between the calculated thermomagnetic properties and the reference data confirms the effectiveness of our theoretical approach. Working with ATOMIC MATTERS MFA revealed its high usefulness. The visual form of calculation results, full 3D interactive CEF potential visualization, intuitive tools for convention and unit recalculation, and the ability to compare data results all make it easy for users to utilize the power of the application very effectively. In conclusion, we confirm that ATOMIC MATTERS MFA is a unique application that combines a package of tools for correctly describing the physical properties of atomic-like electron systems subjected to electromagnetic interactions in real materials. This is an accurate tool for calculating the properties of ions under the influence of the electrostatic potential of definable symmetry and both external and inter-ionic magnetic fields taken as a mean field approximation in a magnetically ordered state.

This paper is the first in a series devoted to the RAl_2 (R=rare earth) compounds family non-free parameters calculations. The obtained set of parameters will be used for calculations of heavy rare earth elements: Gd, Tb, Ho, Er, Tm… in crystal structure RAl_2. The molecular field factor will be recalculated according to de Gennes scaling.

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