THERMAL SINGLE-IONIC MAGNETIC PROPERTIES OF MATERIALS CALCULATED WITH ATOMIC MATTERS MFA COMPUTATION SYSTEM

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ABSTRACT

We present the concept and scientific methods of a new computation system called ATOMIC MATTERS MFA. This computation system is useful for magnetocaloric effect (MCE) estimations for defined materials. ATOMIC MATTERS MFA provides 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 as both Mean Field Approximation (MFA) and the influence of external magnetic fields. ATOMIC MATTERS MFA provides macroscopic properties of materials in different temperature regions, especially around phase transition temperature, such as: magnetic moment (spin and orbit components), localized electron specific heat, localized electron entropy (with a useful tool set for MCE estimations), evolution of energy level positions, and total free energy temperature dependences in a definable temperature region. ATOMIC MATTERS MFA computation system is an extension of the ATOMIC MATTERS application, a system for describing fine electronic structure and predicting basic magnetic and spectral properties of materials.

Keywords: ATOMIC MATTERS, ATOMIC MATTERS MFA, Mean Field Approximation (MFA), crystal electric field (CEF), spin-orbit coupling, Magnetocaloric effect (MCE).

1. INTRODUCTION

The single ionic properties of paramagnetic ions are the core magnetic properties of magnetic materials. Finding active materials dedicated to magnetic refrigeration at room temperature need tools for single ionic properties provides. Therefore, we have created software to perform calculations of fine electronic structure for paramagnetic ions. Our aim was to find and parameterize the most important interactions in atoms and ions in ligand environments. Such parameterization, which comes directly from Crystal Electric Field (CEF) theory[1-3], makes it possible to transfer the influence of local charge surroundings between different ions and predict the magnetic properties of materials in isostructural series [4-6]. This system is called ATOMIC MATTERS. Algorithms and technical details of ATOMIC MATTERS computation system were published at [7] and are also available on the software web page [8], together with hundreds of examples of calculation results for ions from different areas of the periodic table in real, well-known materials. All ATOMIC MATTERS calculations can simulate materials under stable field conditions (both CEF and external magnetic field) and interactions. ATOMIC MATTERS MFA can simulate phase transitions of ionic/atomic systems according to dynamic calculations of the molecular field $\mathbf{B}_{\mathrm{mol}}$, simply defined as:

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

that interacts with ions to induce their magnetic moment. Such self-consistent calculations can be performed after establishing the molecular field factor n_{mol}, which is closely related to the phase transition temperature (T_C or T_N)[9]. Our solution applies to situations in which an unclosed electron 3d/4d/5d/4f/5f subshell interacts with the electrostatic potential of definable symmetry (taken as a CEF) and the external magnetic field and molecular magnetic field of identical neighbors, calculated under Mean Feld Approximation (MFA) methodology.

2. THEORETICAL APPROACH

Our approach, which is applied to both ATOMIC MATTERS and ATOMIC MATTERS MFA computation systems, is deeply rooted in atomic physics. Taking into consideration the individual population of states of fine electronic structure of ions/atoms different temperatures according L. Boltzmann statistics makes it possible to define the temperature dependencies of properties such as:

- full structure of discrete electron levels E_i or E_i (T) for magnetization process in chosen calculation space $|J,J_z>$ or $|L,S,L_z,S_z>$
- Helmholtz free energy F(T), internal energy U(T), magnetic entropy S_{mag}(T)
- formation of magnetic ordered state
- localized electronic contribution to specific heat c_{mol}(T) for temperature dependent energy level states E_i(T) around magnetic phase transition temperature.
- spectra simulations for different methods and conditions, including INS (Inelastic Neutron Scattering)
- magnetic moment and magnetization in ordered state
- spin and orbital contribution to angular momentum of the entire electron subshell
- magnetocrystalline anisotropy constants K_i(T)

For rapid calculations in the thermodynamically stable temperature region, ATOMIC MATTERS offers the following CEF+Spin-Orbit+Zeeman Hamiltonian according to the chosen calculation space of ground multiplet $|J,J_z>$ or ground atomic term $|L,S,L_z,S_z,>$ respectively[11]:

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

or

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

For all Hamiltonians: B^m_n denotes CEF parameters, $\mathbf{O}^m_n$ are Stevens operators, λ-is the spin–orbit constant, g_L and $g_e \approx 2.002324$ are the gyromagnetic factors. For whole ion and for electron respectively, μ_B is the Bohr magneton and $\mathbf{B}_{ext}$ is the external magnetic field.

In all cases, calculations in the $|L,S,L_z,S_z,>$ space are more physically appropriate due to their completeness, but traditional calculations with base $|J,J_z>$ can be also performed by our computation systems for comparisons and rapid estimations [1],[2]. For calculating properties in temperatures around the magnetic phase transition point (by ATOMIC MATTERS MFA), self-consistent methodology for molecular field calculation called Mean Field Approximations(MFA) is applied. The idea of this method is the estimation of direction and value of the magnetic field (molecular field) generated by ions at defined temperature, and calculating the influence of this magnetic field for electronic states structures of ions. According to the chosen calculation space, we define molecular field as:

$$\mathbf{B}_{mol} = -n_{mol}\, g_L \mu_B < \mathbf{J} > \quad \text{or}$$

$$\mathbf{B}_{mol} = -n_{mol}\, \mu_B < \mathbf{L} + g_e \mathbf{S} > .$$

On the basis of calculated electronic structure E_i, 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, 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 only 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_N or T_C of the macroscopic structure of ions. The formal expression of the full Hamiltonian used by ATOMIC MATTERS MFA computation system, according cto the hosen calculation space $|J,J_z>$ or $|L,S,L_z,S_z,>$ respectively, has the form:

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

or

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

The eigenvectors of the Hamiltonian are described according to the selected calculation base by the total momentum quantum numbers $|J,J_z>$ or spin and orbit quantum numbers $|L,S,L_z,S_z,>$. 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]-[5], [8].

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

Where: α indexes directional components, i - numbers the Hamiltonian eigenstates, while $<\mathbf{J}_\alpha>$ represents the expected value of the total angular momentum along the α-axis in the i-th state. 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 $\mathbf{O}^{n}{}_{m}$ operators[10]. Mostly for comparison with traditional calculation results, ATOMIC MATTERS also offers, 2D (x,z) calculation methodology of a simplified model of CEF interactions defined by Stevens $\mathbf{O}^{n}{}_{m}$ operators with real number matrix elements only [1-3],[7],[11].

3. THEORMODYNAMICS

Taking into consideration the possibility of the thermal population of states, we automatically obtain thermal evolution of single ion properties of whole compound[3],[4],[7-11]. Under the thermodynamic principle at a temperature T = 0 K, 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:

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

where $N_0 \approx 6.022.10^{23}$ mol^{-1} (Avogadro constant) and Z(T) is the statistical sum of states:

$$Z(T) = \mathrm{Tr}\left(\exp\left(-\frac{\hat{\mathbf{H}}}{k_B T}\right)\right) = \sum_i \exp\left(-\frac{E_i(T)}{k_B T}\right)$$

Knowing the statistical sum of the states, we can determine the Helmholtz free energy F(T):

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

which makes it possible to estimate the internal energy U(T) of the system:

$$U(T) = F(T) - T\left(\frac{\partial F(T)}{\partial T}\right) = -k_B T \frac{\partial}{\partial T}\left(\frac{F(T)}{k_B T}\right)$$

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:

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

It make it possible to calculate entropy according to definition:

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

However, for general correctness, due to the fact that open subshell ions are in a self-organized molecular field, their magnetic moment changes with temperature. Bearing in mind that each eigenstate of the CEF Hamiltonian is related to its magnetic moment, the total moment of a strongly correlated electron system at a given temperature is the resultant moment of occupied states calculated with the inclusion of the Boltzmann weight and:

$$M_\alpha(T) = g_L \mu_B \sum_i N_i(T) < \Gamma_i(T) | \mathbf{J}_\alpha | \Gamma_i(T) >$$

or

$$M_\alpha(T) = \mu_B \sum_i N_i(T) < \Gamma_i(T) | (\mathbf{L}_\alpha + g_e \mathbf{S}_\alpha) | \Gamma_i(T) >$$

where α-indexes directional components, i-numbers the Hamiltonian eigenstates, while $<\mathbf{J}_\alpha>$ and $<|(\mathbf{L}_\alpha + g_e \mathbf{S}_\alpha)>$ represent the expected values of the total angular momentum operator defined in different spaces. Such magnetic moment calculations, under influence of a freely defined external magnetic field and internal dynamic calculated molecular field can be achieved by ATOMIC MATTERS MFA.

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.

4. EXAMLES OF RESULTS

According to the described methodology, we present the calculations results for well-known magnetic magnetocaloric compound $DyAl_2$. All used calculated parameters used for calculations are shown on the plots apart from CEF parameters of cubic field taken from[12] : $B_4 = -5.5 \cdot 10^{-5}$meV and $B_6 = -5.6 \cdot 10^{-7}$ meV.

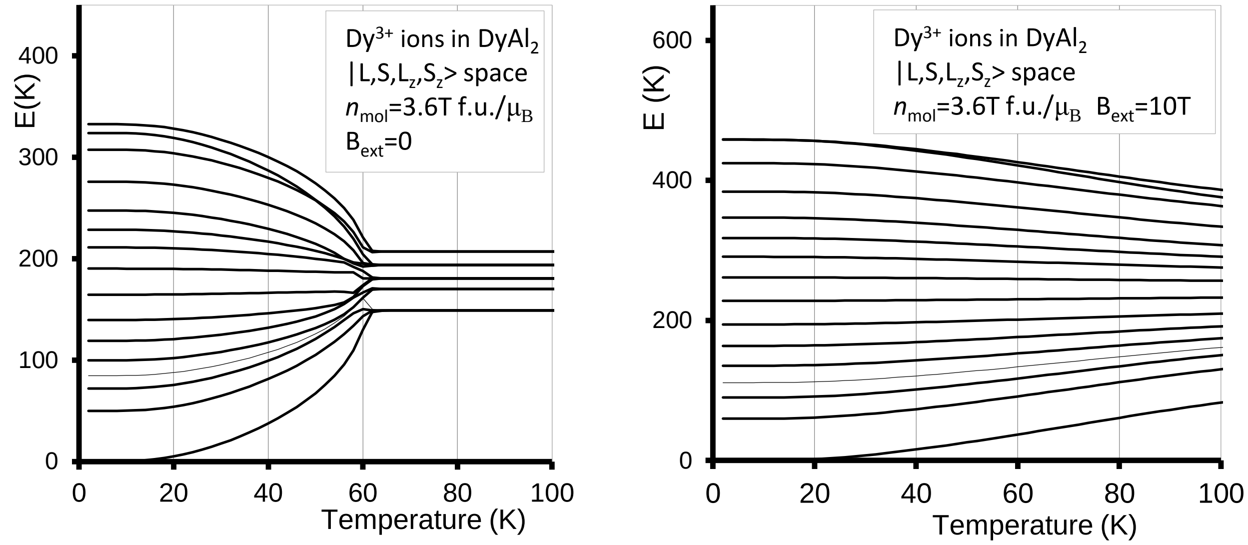

Fig1. Low energy electronic level structure, near ground state, calculated for Dy^{3+} ions in $DyAl_2$, calculated by ATOMIC MATTERS MFA in |L,S,Lz,Sz> space under influence of molecular magnetic field, external magnetic field B=0 and B=10T and CEF with parameters taken from [12].

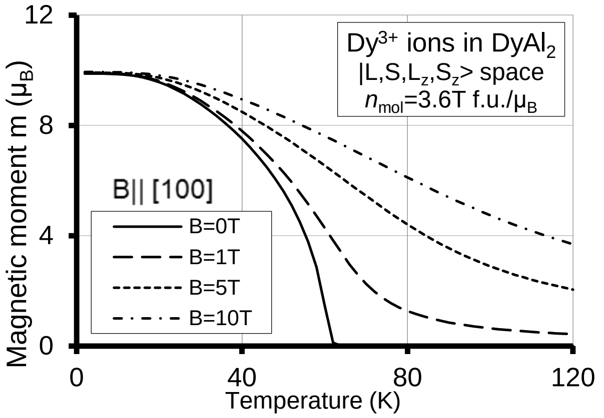

Fig2. Magnetic moment vs. temperature of Dy^{3+} ions in $DyAl_2$, calculated by ATOMIC MATTERS MFA in |L,S,Lz,Sz> space under influence of molecular magnetic field, CEF with parameters taken from [12] and various external magnetic field.

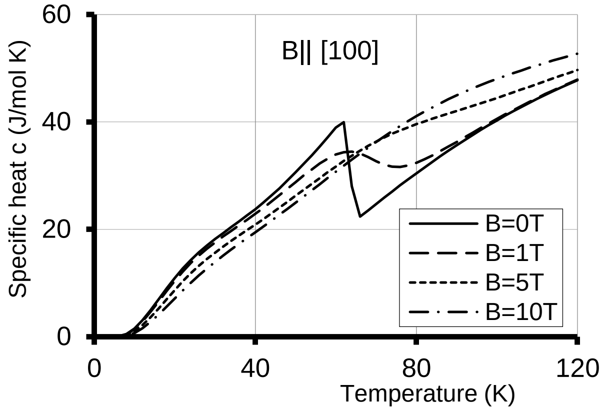

Fig3. 4*f* components of molar specific with Debye component (θ=380K) vs. temperature of Dy^{3+} ions in $DyAl_2$, calculated by ATOMIC MATTERS MFA in |L,S,Lz,Sz> space under influence of molecular magnetic field, CEF with parameters taken from [12] and various external magnetic field parallel to [100] axis

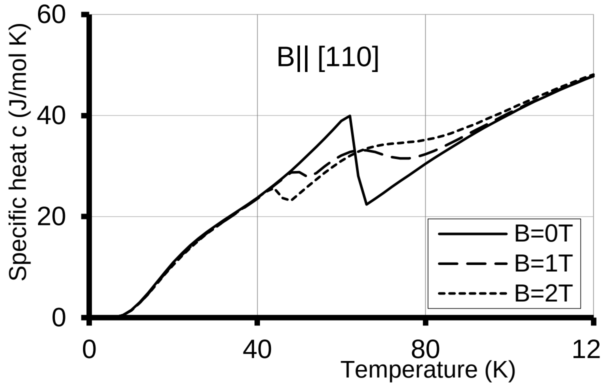

Fig4. 4*f* components of molar specific with Debye component (θ=380K) vs. temperature of Dy^{3+} ions in $DyAl_2$, calculated by ATOMIC MATTERS MFA in |L,S,Lz,Sz> space under influence of molecular magnetic field, CEF with parameters taken from [12] and various external magnetic field parallel to [110] axis.

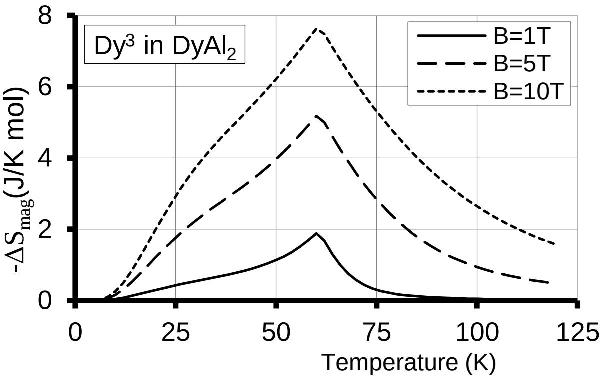

Fig5. 4*f* entropy, calculated under influenxe of external magnetic field parallel to [100] axis for Dy^{3+} ions in $DyAl_2$, in |L,S,Lz,Sz> space under influence of molecular magnetic field, CEF with parameters taken from [12] and various external magnetic field parallel to [100]axis.

5. CONCLUSIONS

Selected calculations of $DyAl_2$ thermal dependent properties were performed with ATOMIC MATTERS MFA. The calculation parameters were taken from references [12]. We obtained excellent agreement with experimental data from [12] and [13]. All calculations made it clear that ATOMIC MATTERS MFA computation system is extremely useful. The visual form of calculation results and full 3D interactive CEF potential visualization make it easy for the user to utilize the power of the application very effectively. From a theoretical point of view, we conclude: In all cases the $|L,S,L_z,S_z>$ base is better for precise magnetism calculations and spectra recognition. Calculations on complex number matrices always produce more precise magnetic simulations. Full, correct directional magnetic information is provided by calculations on complex number matrices only. In general, base |J.Jz>, which is the most commonly used for calculation of R ions, and real number matrix Hamiltonians should be chosen for comparisons and rapid calculations only, because it offers approximate results with intermediate scientific value.

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