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Predictions of thermomagnetic properties of Laves phase compounds: $TbAl_2$, $GdAl_2$ and $SmAl_2$ performed with ATOMIC MATTERS MFA computation system

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ABSTRACT

Recent calculations of properties of $TbAl_2$ $GdAl_2$ and $SmAl_2$ single crystals, performed with our new computation system called ATOMIC MATTERS MFA are presented. We applied localized electron approach to describe the thermal evolution of Fine Electronic Structure of Tb^{3+}, Gd^{3+} and Sm^{3+} ions over a wide temperature range and estimate Magnetocaloric Effect (MCE). Thermomagnetic properties of $TbAl_2$, $GdAl_2$ and $SmAl_2$ were calculated based on the fine electronic structure of the $4f^8$, $4f^7$ and $4f^5$ electronic configuration of the Tb^{3+} and Gd^{3+} and Sm^{3+} ions, respectively. 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 $4f$-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 literature and recalculated for universal cubic parameters set for the RAl_2 series: $A_4 = +7.164\ Ka_0^4$ and $A_6 = -1.038\ Ka_0^6$. Magnetic properties were found to be anisotropic due to cubic Laves phase C15 crystal structure 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.

1. Introduction

One of the biggest challenges in materials science is understanding and controlling the microscopic quantum mechanisms responsible for controlling material entropy through external magnetic field change processes. Our calculation methodology makes it possible to describe the thermomagnetic properties of magnetic materials in large temperature scale such as: magnetic entropy, specific heat, single ionic magnetocrystalline anisotropy and magnetic moment direction and value of R ions (R = Rare Earth). Obtained thermomagnetic properties of materials are the consequence of thermal population of calculated Fine Electronic Structure of $4f^n$ electronic system of R^{3+} ions. We decided to test our approach for $TbAl_2$ $GdAl_2$ and $SmAl_2$ compounds. The material series RAl_2 compounds are intermetallic materials with interesting thermomagnetic properties [3]. In other words, the RAl_2 series of compounds are fascinating due to their large magnetocaloric entropy changes under external magnetic fields. This large change in MCE (Magnetocaloric Effect) is especially attractive in magnetic refrigeration due to its potential environmental friendliness compared to traditional gas refrigeration. We present results of simulations of thermomagnetic properties of some RAl_2 compounds performed with our new computation system called ATOMIC MATTERS MFA [1,2]. A few calculation results for $TbAl_2$ compound are compared with experimental data taken from the literature [3–6] and for $GdAl_2$ from papers [6,7]. All the lanthanides combine with aluminum to form RAl_2 compounds with the same crystalline structure [3]. All RAl_2 compounds are ferromagnetic at low temperatures [3]. RAl_2 crystals have the so-called cubic Laves phase C15 structure, while the point symmetry for rare earth ions is $\bar{4}3m$. The elementary cell of the crystal structure of Laves phase is presented in Fig. 1. The CEF (Crystal Electric Field) parameters describing the multipolar charge interaction of R ions in the crystal surrounding in this structure was agreed for all compounds and established according to studys of the $DyAl_2$ compound [3] for: $A_4 = +7.164\ Ka_0^4$ and $A_6 = -1.038\ Ka_0^6$. We decided to predict the properties of $TbAl_2$ and $GdAl_2$ completely without free parameters;

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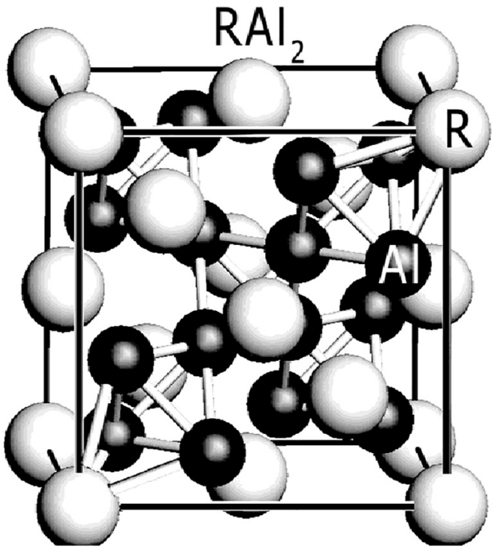

Fig. 1. Cubic elementary cell of RAl_2 Laves phase C15 crystals. Note: We present results of our calculations in atomic units ($a_o = 5.291772 \times 10^{-11}$ is Bohr radius). For convenient comparison of thermal properties of materials with electronic energy level structure of the R^{3+} ion, the energy unit is K (Kelvin); 1 K = 0.861733 meV = 1.38040×10^{-23} J.

therefore, we used the established cubic CEF and molecular field factor n_{mol} that were recalculated from $DyAl_2$.

2. Computation system

All calculations for $TbAl_2$ and $GdAl_2$ were performed with ATOMIC MATTERS MFA computation system. This extension of the ATOMIC MATTERS application [1] describes fine electronic structure and predicts basic magnetic and spectral properties of materials in a paramagnetic state. ATOMIC MATTERS MFA computation system [2] 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 both as dynamic Mean Field Approximation (MFA) and the influence of established external magnetic field $\mathbf{B}_{ext}$ [2]. ATOMIC MATTERS MFA calculates macroscopic properties of materials in defined temperature regions, especially around the phase transition temperature: 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 and more.

To enhance ease of use and efficiency, both calculation systems implement an advanced Graphic User Interface (GUI) with a system of hierarchical tabs for managing calculation results, 3D interactive visualizations of potentials and fields based on Open Graphics Library (OpenGL), intuitive tools and databases. More up-to-date information on features of Atomic Matters computation systems are available on our web page [8].

3. Theoretical background

ATOMIC MATTERS MFA computation system calculation methodology is deeply rooted in atomic physics. Taking into considerationindividual population of states of fine electronic structure of ions/atoms at different temperatures according to Boltzmann statistics makes 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:

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

which 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 $|LS,L_z,S_z>$, respectively [1]:

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

or

$$\begin{aligned} H_{LS} &= H_{CEF} + H_{S-O} + H_{Zeeman} \\ &= \sum_n \sum_m B_n^m \hat{\mathbf{O}}_n^m(L, L_z) + \lambda \mathbf{L} \cdot \mathbf{S} + \mu_B(\mathbf{L} + g_e\mathbf{S}) \cdot \mathbf{B}_{ext} \end{aligned} \tag{3}$$

For all Hamiltonians B_n^m denote CEF parameters, $\mathbf{O}_n^m$ are Stevens operators, λ is the spin–orbit constant, and g_L and $g_e \approx 2.002319$ are the gyromagnetic factors of the whole ion or single electron, respectively, μ_B is the Bohr magneton and $\mathbf{B}_{ext}$ is the external magnetic field. In all cases, calculations in the $|LS,L_z,S_z>$ space are more physically appropriate due to their completeness, but traditional calculations in $|J,J_z>$ space can also be 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 to estimate the direction and value of the magnetic field (molecular field) generated by ions at a defined temperature, and to calculate 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 4*f* electronic subshell multiplied by the molecular field, inter ionic exchange factor n_{mol}:

$$\mathbf{B}_{mol} = -n_{mol} g_L \mu_B \langle \mathbf{J} \rangle \tag{4}$$

or

$$\mathbf{B}_{mol} = -n_{mol} \mu_B \langle \mathbf{L} + g_e \mathbf{S} \rangle \tag{5}$$

where the gyromagnetic factors are g_L and $g_e \approx 2.002319$. On the basis of the calculated electronic level structure $E_i(T)$, the directional components of magnetic moments are established for all described ions. This means that Hamiltonian matrix diagonalization is performed for all defined temperature steps recurrently. This is in contrast to simple ATOMIC MATTERS calculations [1], which diagonalize one matrix in 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 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: $|J,J_z>$ or $|LS,L_z,S_z>$, respectively, has the form:

$$\begin{aligned} H_{J\,mol} &= H_J + H_{mol} \\ &= +\sum_n \sum_m B_n^m \hat{\mathbf{O}}_n^m(J, J_z) + n_{mol} g_L^2 \mu_B^2 \left(-\mathbf{J}\langle \mathbf{J} \rangle + \frac{1}{2} \langle \mathbf{J} \rangle^2 \right) + g_L \mu_B \mathbf{J} \cdot \mathbf{B}_{ext} \end{aligned} \tag{6}$$